TECHNICAL PROGRESS REVIEWS

REACTOR FUEL PROCESSING

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

JULY 1958 VOLUME 1 NUMBER 3

TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

a review of recent developments *prepared by*

ARGONNE NATIONAL LABORATORY

JULY 1958 VOLUME 1 NUMBER 3

ATOMIC ENERGY COMMISSION • UNITED STATES OF AMERICA

foreword

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission, Division of Information Services. It is the third issue of this series, intended to assist those interested in keeping abreast of important developments in this field. In each review it is planned to cover those particular subjects in which significant new results have been obtained. The review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date as circumstances warrant.

Interpretation of results, where given, represents the opinions of the editors who are personnel of Argonne National Laboratory, Chemical Engineering Division. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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contents

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REACTOR FUEL PROCESSING

COMMERCIAL ASPECTS OF FUEL PROCESSING

On Mar. 12, 1958, the AEC put into the *Federal Register*[1] conversion charges relating to chemical process service. On Feb. 18, 1957, the Commission announced[2,3] that, until commercial facilities are set up to do the work at reasonable prices, it will furnish a processing service for the recovery of source and special nuclear materials contained in irradiated fuel elements or blanket materials removed from privately operated reactors. The Commission will carry out the processing at firm charges under individually negotiated contracts. The earlier announcement pointed out that the processing system would yield purified nitrate salts of uranium and plutonium and that there would be additional charges to be specified later for conversion of these products to form uranium hexafluoride and plutonium metal for which Commission prices have been established. These additional charges are as follows:

1. Conversion of purified low-enrichment uranyl nitrate (5 wt.% or less of U^{235} in total uranium) into uranium hexafluoride (UF_6), \$5.60 per kilogram of contained uranium.
2. Conversion of purified high-enrichment uranyl nitrate (more than 5 wt.% of U^{235} in total uranium) into uranium hexafluoride (UF_6), \$32.00 per kilogram of contained uranium.
3. Conversion of purified plutonium nitrate to plutonium metal, \$1.50 per gram of contained plutonium.

In Vol. 1, No. 2, of *Power Reactor Technology* (a companion review to this series), Walter H. Zinn, former Director of Argonne National Laboratory (ANL), in discussing a Hanford report on the plutonium recycle program which evaluates plutonium relative to U^{235} (at \$17.11 per gram) in terms of the energy output per gram, said:

> On this basis pure Pu^{239} should be worth \$14.10 per gram. The decrease relative to U^{235} is due to the circumstance that a greater fraction of the Pu^{239} is lost by neutron capture. The value of reactor grade plutonium which would contain only about 81 per cent fissionable isotope would be \$11.42 per gram. Actually in a competitive market the price of plutonium would very probably find a lower value relative to U^{235} because of its other disadvantages. Furthermore, it is hardly reasonable to base the economic value of plutonium on that of pure U^{235} since it is unlikely that many large power reactors will use pure U^{235}. It seems much more probable that plutonium in the thermal reactor field will eventually compete with slightly enriched uranium, for which the price lies in the range of \$10 to \$13 per gram of U^{235}.

In this same review Zinn also said that it is evident that attractively low fuel costs cannot be obtained with throw-away fuel of enrichment appreciably higher than the natural ratio. The hope for low fuel cost with higher enrichments rests on the possibility of reprocessing the fuel after it has been discharged from the reactor and recovering the unburned U^{235} as well as any fissionable product that has been formed by conversion. The net fuel cost will depend upon the cost of reprocessing, and low fuel costs can be obtained only if the reprocessing cost is low. He also said that, despite the relatively low reprocessing cost which is indicated in the Commission announcements, reactors using fuel enrichments in the neighborhood of 2 per cent or more must have quite good neutron economy and a high conversion ratio to approach a fuel burn-up cost, including reprocessing, of 1 mill or less per kilowatt hour.

During this period the British announced some guaranteed prices for use in their international trade. They guarantee prices of fuel elements as follows: selling price at \$56,000 per ton; buy-back price, with a guaranteed life of 3000 Mwd per ton, at \$14,000 per ton. This amounts to a net cost, exclusive of inventory,

of $42,000 per ton; this net cost, divided by 3000 Mwd per ton, equals 0.6 mill per thermal kilowatt hour per complete fuel cycle. At 30 per cent thermal efficiency this equals 2 mills per kilowatt hour electric. Also the buy-back price is guaranteed at $14,000 per ton for 3000 Mwd per ton elements (3000 Mwd per ton natural uranium elements contain approximately 2000 g of plutonium per ton); therefore this price is approximately $7.00 per gram of contained plutonium. This means that they are selling finished (machined, canned, tested, etc.) fuel at $6.70 to $7.80 per gram of fissionable material (U^{235}) and are willing to pay $7.00 per gram of plutonium returned. To this price must be added the cost of chemical processing, waste disposal, conversion to metal, and fabrication into finished form. It might be noted that for reactor fuel, especially in thermal reactors on which the United Kingdom is concentrating, the high alpha (σ_C/σ_f) of plutonium makes it a less desirable fuel than U^{235}.

The British, in an agreement with Italy concerning the reactor they are supplying them, also made the following statement:[4] "The cost of shipping irradiated fuel back from Italy to the United Kingdom should be about £1000 ($2800) per ton, i.e., 2204 lb. It should not under any circumstances exceed $4200 per ton."

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2. *Federal Register*, Vol. 22, No. 48, F.R. Doc. 57-1820, p. 1591, Mar. 12, 1957. (Available from the U. S. Atomic Energy Commission, Office of Industrial Development, Washington 25, D. C.
3. *Reactor Fuel Processing*, Vol. 1, No. 1, February 1958. (Available from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.)
4. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 5, No. 3, 1958.

Work continues on the development of methods of decladding, dissolution, and head-end treatments for a wide variety of fuels. Decladding may be accomplished mechanically or chemically; dissolution is performed chemically, the exact treatment depending upon the composition of the fuel.

Disassembly

Mechanical Processing

Many of the newer fuels are clad with materials that will not dissolve in HNO_3 as the fuel will. Therefore the removal or destruction of the clad by mechanical processing will sometimes permit conventional HNO_3 dissolution of the fuel material. Three approaches to mechanical processing of nonproduction fuels are in the preliminary evaluation stage.[1,2] These are sawing, shearing, and pulverizing. Various sawing techniques and procedures will be evaluated by cutting simulated uranium dioxide fuel elements composed of fused and sintered alkaline-earth porcelain, jacketed in zirconium or stainless steel. A carbide-tipped saw blade, a friction blade, abrasive wheels, and diamond wheels will be tested.

A mechanical processing feasibility study has been made by American Machine & Foundry Co.[3] On the basis of information already received by them, it was decided that preliminary dismantling that did not involve exposure of fuel material could be done in air or water, depending upon the specific problems involved for each fuel type. For operations involving exposure of the core material, the concept of local underwater "bathtub" operation was adopted. Eight different types of machines have been considered in this study, including a Universal sawing machine, a shake-out machine (of specific interest to the Atomic Power Development Associates (APDA) core), a shearing machine, a hydraulic pressure-removal device for expulsion of fuel from jackets, an end-cap-removal machine, a fuel-slug-removal unit, a tube peeler, and a lathe type spiral grooving machine.

For handling oxide elements, crusher rolls to pulverize the core of oxide elements followed by tube shearing may be best. Transfer of oxide to a dissolver is envisioned by a steam jet that collects the oxide from a sump.

Roll Decladding Studies. Aluminum jackets could not be completely removed from Savannah River slugs by rolling in a Mackintosh-Hemphill derodding machine. Sections of the jacket were freed from the uranium core, but the majority remained bonded after 10 to 27 passes through the three sets of rollers. The number of passes required to dejacket reject slugs varied from three to seven, and only an occasional slug had bonded sections that would break. Circular scoring the aluminum cladding thickness caused the end caps to break off in three to four passes through the machine. Longitudinal scoring on either side or spiral scoring to one-half the cladding thickness did not improve decladding. Circular scoring at 2-in. intervals through the cladding allowed the removal of the clad in three passes.

Ten aluminum-silicon bonded aluminum jackets removed from Savannah River slugs by the Mackintosh-Hemphill machine were dissolved, with a uranium loss of 0.07 per cent.

Rolling operations on simulated Yankee atomic fuel rods (stainless steel clad, 2.6 per cent enriched UO_2) resulted in work being applied on the quartered sections of the $\frac{1}{4}$-in. tubing and breaking through the clad at these points. The end caps were not removed by the machine since work could not be applied to the entire cladding. It was concluded that the machine will not successfully declad fuels with ferruled sections of spacer tubes on the cladding.

Chemical Processing

Various processes are now under study at several AEC sites,[4] which may be used for either the removal of cladding materials or the

complete dissolution of fuels not soluble in HNO_3 alone. Two of these processes (Zircex and Darex) have been described in the literature[5] and were mentioned in Vol. 1, No. 1, of this Review.

In Zircex process studies,[6] Pressurized Water Reactor (PWR) blanket fuel rods were dejacketed with anhydrous HCl, with losses as indicated in the following tabulation:

Dejacketing temp., °C	Dejacketing time, hr	Sublimation loss, %	Insolubles loss, %
600	$1\frac{1}{2}$	0.005	0.002
725	1	0.08	0.006

Adsorption of chlorine by the unreacted uranium dioxide pellets was approximately 1 per cent. Chlorination of zirconium alloy fuels by constant-pressure chlorine gas fed into a closed system was controlled by the rate of heat dissipation from the chlorinator.

A unit capable of handling irradiated PWR blanket fuel elements has performed well in preliminary nonradioactive runs.[7] Zirconium tetrachloride was removed from the hydrochlorinator exit gas stream by a high-temperature reaction with solid sodium chloride to form a solid chloro-zirconate. The alloy (85.4 per cent uranium, 10.6 per cent niobium, 4 per cent zirconium) dissolved at a rate of 10 mg/(cm^2)(min) in $3ZrCl_4 \cdot 2POCl_3$. The insoluble uranium loss after HNO_3 dissolution of the residue was 0.2 per cent.

Fluidization has been used to remove heat from the hydrochlorinator and the zirconium chloride desublimer. An initial fluidization air velocity of 0.22 ft/sec was used. At this gas velocity the bed expansion was 19 per cent, and the pressure drop across the bed was 12 lb/sq ft.

A specimen of uranium–10 per cent niobium reacted with HCl at 400°C at a rate of 0.67 mg/(cm^2)(min), with a uranium loss of 0.016 per cent to the sublimate.[8] About two-thirds of the 3600-g sections of a 12-plate assembly (99 per cent Zircaloy, 1 per cent uranium) reacted with HCl in 15.5 hr at 500°C. Uranium losses were 1.1 per cent to the sublimate and 0.4 per cent as insolubles in 10*M* HNO_3. In a run on a high uranium-zirconium-niobium alloy specimen in which air and moisture were excluded, HNO_3 insoluble uranium losses were only 0.005 per cent. In preliminary experiments on the system $3ZrCl_4 \cdot 2POCl_3$, chlorination rates were favorable, especially for high uranium-zirconium-niobium alloys.

Following hydrochlorination of these alloys at 400 and 600°C, greater than 99 per cent of the uranium was recovered in an aqueous nitrate solution.[9] No finely divided metallic residues were observed after hydrochlorination, and no violent reaction during HNO_3 dissolution of the residues was noted.

In Darex process studies[8] the initial dissolution rate of uranium dioxide in 3*M* to 6*M* HNO_3 containing 1*M* and 2*M* HCl was 21 to 51 mg/(cm^2)(min). Off-gases from uranium dioxide dissolution contained a higher proportion of chloride species and a lower proportion of nitric oxide (NO) than those from stainless steel. When the nitric oxide to chlorine mole ratio was 2, chlorine and nitrogen oxides were almost completely absorbed. A large portion of the rectifier was operated at a low temperature, and oxygen, 30 per cent in excess of that required to oxidize all the nitric oxide to nitrogen dioxide, was bled in.

Engineering scale tests have been made on the rectification of dissolver off-gas from the Darex process.[9] These have indicated that it is not feasible to obtain pure water overhead from the rectifier. The rectifier has therefore been replaced with a downdraft condenser, and in batch experiments, on removal of chloride from dissolver solutions, more than one volume of 15.8*M* HNO_3 was necessary to oxidize the chloride and to remove it from solution. Three unsteady-state runs in the Darex loop[7] indicated that approximately 15 per cent of the make-up HNO_3 had to be added directly to the dissolver to sustain dissolution. Losses of chloride and nitrate to the off-gas were 3 to 12 and 2 to 3 per cent, respectively. Chloride was stripped from the dissolver product down to 70 to 850 ppm.

Another process for the removal of Zircaloy or zirconium jackets is the Zirflex process. This makes use of an aqueous solution of ammonium fluoride–ammonium nitrate.[2] Experiments to date have used 10 to 20 liters of boiling 6*M* ammonium fluoride–0.5*M* ammonium nitrate to dissolve 1 to 1.5 kg of scrap Zircaloy tubing or sheet metal. The results of these studies are (1) terminal dissolution rates of unoxidized metal were lower than expected, (2) production of copious quantities of precipitates resulted, and (3) dissolution of a metal

charge that was deliberately subjected to oxidizing conditions was very slow.

Measurement of the ammonia evolved during the dissolution of Zircaloy-2 in Zirflex solutions[10] disclosed that 4.9 moles of ammonia is evolved per mole of zirconium dissolved. This, together with the observation that no more than minor amounts of nitrogen, hydrogen, or oxides of nitrogen are evolved in the reaction, suggests that the dissolution process in 6*M* ammonium fluoride solutions containing 0.5*M* or greater of ammonium nitrate can be represented by the equation

$$\mathrm{Zr(solid)} + 6.5\mathrm{NH_4^+} + 6\mathrm{F^-} + 0.5\mathrm{NO_3^-} \rightarrow \mathrm{ZrF_6^{-2}} + 2\mathrm{NH_4^+} + 5\mathrm{NH_3(gas)} + 1.5\mathrm{H_2O}$$

A uranium–9 wt.% zirconium alloy was attacked at an appreciable rate by a boiling solution of 6*M* ammonium fluoride–1*M* ammonium nitrate. With 6*M* ammonium fluoride the alloy was attacked at an average rate of 0.3 g/(hr)(cm^2) over a 3-hr interval, but the rate decreased to 0.2 g/(hr)(cm^2) during the second 3-hr interval, presumably because of the formation of a protective coating of insoluble uranium(IV) fluorides. With 6*M* ammonium fluoride–1*M* ammonium nitrate, the rate of attack remained constant at 0.6 g/(hr)(cm^2) over three consecutive 3-hr intervals, and the insoluble uranium salts showed no tendency to adhere to the alloy sample. It should be noted that a rate of 0.6 g/(hr)(cm^2) is quite appreciable, nearly as high as the rate of dissolution of uranium metal in 8*M* HNO_3. This observation suggests the possibility of processing uranium-zirconium alloys containing moderate amounts of uranium by dissolving the zirconium and simultaneously converting the uranium quantitatively to insoluble fluorides that can be separated from the zirconium-containing supernatant, converted to hydrous oxides by alkaline metathesis, and finally dissolved in HNO_3 for processing.

In additional studies on aqueous cladding[8] dissolution alternate to HNO_3, zirconium and Zircaloy-2 dissolved in 2*M*, 5*M*, 9*M*, and 12*M* HF at 90°C at practical rates even when the acid was 75 per cent saturated with dissolved zirconium. Dissolution rates for uranium–10 per cent molybdenum and uranium–10 per cent niobium under these same conditions were 0.11 to 0.58 and 0.13 to 0 mg/(cm^2)(min), respectively. $ZrF \cdot 3H_2O$ was precipitated from these solutions almost quantitatively by the addition of acetone.

The attack of HNO_3-HF on Zircaloy-2 was decreased sharply by increasing the concentration of zirconium(IV) in the acid. As a dissolvent, 13*M* HNO_3–0.004*M* HF did not appear practical[6] for Zircaloy-2. Dissolution rates of Zircaloy-2 and uranium–10 per cent niobium in 9*M* HF were 284 and 0.031 mg/(cm^2)(min), respectively, indicating the practicability of removing Zircaloy jackets from uranium-niobium alloys with this reagent.

Fuel Dissolution

In HNO_3 dissolution studies[11] dingot (direct ingot) uranium has a slower dissolution rate in HNO_3 than ingot uranium. It differs chiefly from ingot uranium in that it has (1) a much lower carbon content, (2) a high purity, and (3) a larger grain size. The data from experiments designed to isolate the effects of these variables showed no good correlation with carbon content but indicated the slow dissolution rate for dingot uranium as compared to ingot uranium was due to the larger grain size. It was suggested that the grain size might be reduced by a different heat-treating schedule or by small additions of elements that promote nucleation. Dissolution rates[1] for ingot, dingot, and high-carbon dingot uranium in 8*M* HNO_3 were 0.75, 0.27, and 0.27 g/(cm^2)(hr), respectively.

A laboratory dissolution experiment was carried out to define the solution parameters most important to uranium dissolving rates. Uranyl nitrate–nitric acid solutions in the range of 1*M* to 3*M* HNO_3 and 5*M* to 9*M* total nitrate were used with small amounts of H_2SO_4 and sodium nitrite. Principal findings were (1) the addition of 0.1*M* H_2SO_4 or 0.2*M* sodium nitrite did not increase the dissolving rate significantly (within ±12 per cent), (2) the dissolving rate depended primarily on the total nitrate concentration (a factor of 15 to 20 in the range studied) and secondarily on the free HNO_3 concentration (a factor of 2 to 3 in the range studied), and (3) there was evidence of an induction period at the beginning of the dissolution. Further experiments to define more closely the effects of nitrate ion in free HNO_3 have been planned.

A process for the complete dissolution of stainless-steel jacketed fuel elements involves the utilization[2] of a mixture of HNO_3 and HF. It is possible that the material of construction for this vessel might be compatible with Zirflex solutions. If this were the case, a single dissolution vessel would be capable of handling both stainless-steel and zirconium jacketed elements. Preliminary dissolution and corrosion rates are tabulated below. These are Huey type tests and involve a 1-hr exposure of the metal to the boiling solution.

Dissolution rate, mils/hr

Solution	304L	Haynes 25	Zircaloy-2
5M HNO_3, 1M HF	1.02	0.055	85
2M HNO_3, 1M HF	2.15	0.040	80
1M HNO_3, 1M HF	4.00	0.050	70
5M HNO_3, 2M HF	2.07	0.105	100
2M HNO_3, 2M HF	4.75	0.120	100
1M HNO_3, 2M HF	6.93		100

These data indicate that the dissolution of 304L stainless-steel clad can be carried out in HNO_3-HF systems with an HNO_3 concentration between 0.5M and 1M and that satisfactory dissolution rates can be obtained at HF concentrations as low as 1M.

Sulfex Process

Sulfuric acid dissolution (Sulfex process) of reactor fuels containing stainless steel is the oldest method proposed for chemical head-end treatment for processing this type fuel. In laboratory scale studies[9] hydrogen peroxide, chromium trioxide, manganese dioxide, or sodium dichromate contributed to uranium losses up to 95 per cent during H_2SO_4 dissolution of stainless steel. Essentially all radioactivity in the H_2SO_4 decladding solution was due to activated components of the stainless-steel jacket. A total of 2.4 per cent of the beta and 9.1 per cent of the gamma activity from mixed fission products was leached from a calcium sulfate cake made by neutralizing H_2SO_4 decladding solution with lime. Uranium was quantitatively recovered on Dowex-1 resin from a simulated stainless-steel sulfate decladding solution, whereas plutonium tracer was not sorbed in the same experiment.

In additional studies,[7] type 304L stainless steel dissolved at an average rate of 4 mg/(cm^2)(min) in refluxing (105 to 110°C, 2M H_2SO_4), the rate remaining relatively constant until the acid concentration decreased to about 2M and the stainless-steel concentration reached a value of 100 to 110 g/liter (about 2M). Beyond this point dissolution products precipitated on cooling, and the dissolution rate decreased rapidly.

Other studies[12] on the Sulfex process show that a 400 per cent excess of 6M H_2SO_4 is required to dissolve low-manganese low-carbon type 347 stainless steel, whereas ordinary type 347 stainless steel will dissolve rapidly in 100 per cent excess of 6M H_2SO_4.

Dissolution rates of sintered 96 per cent thoria – 4 per cent urania pellets[9] were fairly constant, 5.4 to 6.2 mg/(cm^2)(min) in 16M HNO_3 containing 0.04M to 0.05M fluoride. Insoluble thorium tetrafluoride formed at lower fluoride concentrations. Further dissolution studies on the same material[7] indicated that solutions 1M to 2M in dissolved thorium can be obtained in 1 to 6 hr, depending upon the solution volume to fuel surface area ratio. Dissolution rates dropped markedly between 0.8M and 1.4M dissolved thorium.

Zirflex Process Applied to Plutonium-Uranium-Aluminum Alloys

A sample of 1.5 wt.% plutonium – aluminum alloy was exposed for 3.5 hr to a boiling solution containing 0.8M $(NH_4)_2ZrF_6$ and 1.2M ammonium fluoride. The plutonium content of the boiling solution increased gradually from 0.07 mg plutonium per liter (at 15 min) to 0.16 mg plutonium per liter at 3.5 hr. The latter value is lower by a factor of 15 than the result obtained in an earlier experiment employing 6M ammonium fluoride. A white coating formed on the alloy, but the bulk precipitate that had been seen in the earlier experiment was not observed. Furthermore, the uranium proved more soluble in the cooled supernatant than would have been expected from solubility data obtained in the absence of aluminum. It is presumed that complexing of fluoride by dissolved aluminum reduced the free fluoride concentration, thereby increasing the zirconium solubility.[1]

Exposure of a plutonium-uranium alloy (Pu:U = 1.1×10^{-3}) to boiling solutions of 6M ammonium fluoride containing various concen-

trations of dissolved zirconium resulted in a lower relative loss of plutonium than of uranium. This was shown by the fact that ratios of plutonium to uranium in the boiling solution were lower than that of the original alloy, ranging from 7×10^{-4} in $6M$ ammonium fluoride to 2×10^{-4} in $6M$ ammonium fluoride containing $0.86M$ zirconium.

Removal of Zirconium from Dissolver Solution from Sulfex Process

A proposed treatment for removal of zirconium from Sulfex process dissolver solution[13] is to add carbonate to the sulfate solution to complex uranium and zirconium. Upon heating, the bulk of the zirconium precipitates out as the hydroxide, whereas the uranium remains complexed. The zirconium may then be removed by filtration. Since the uranium is now ionic, it can be separated from cationic fission products by ion exchange. An experiment was run with uranium in carbonate solution containing cesium spiked with Cs^{137} tracer which was run through a cation-exchange column. Cesium remained in the column, whereas uranium passed through.

At Oak Ridge National Laboratory (ORNL), attempts to remove the zirconium selectively from the zirconium-uranium dejacketing solution by precipitation prior to ion-exchange recovery of the uranium were unsuccessful.[8] Uranium and zirconium carbonates have essentially the same adsorption affinity for anion-exchange resin.

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It is the purpose of this section to cover new work on existing separations processes and on proposed processes. The general areas covered are solvent extraction, precipitation, ion exchange, volatility, and pyrometallurgical processing, processing for homogeneous reactor systems, corrosion, and instrument and equipment development.

During this quarter, current data[1] on the fission yields of U^{235}, U^{233}, Pu^{239}, Th^{232}, and U^{238} for both thermal and fast fission became available.

Solvent Extraction

Redox and Purex are the major liquid-liquid extraction processes in use today. The Redox process employs a methyl isobutyl ketone solvent, and Purex employs a solvent of tributyl phosphate (TBP) diluted with a kerosene fraction. Various modifications of these processes have been adapted to enable the processing of alloys and ore leach liquors. Some equipment developments and a discussion of recent criticality data are presented. The high extractive power of certain amines has led to a series of interesting applications. Notes are included on a number of studies of radiation damage to process solutions.

Purex Flow Sheet Studies

The goal of present Purex flow sheet studies is to develop a one-cycle solvent-extraction process that accomplishes the major part of the necessary fission-product decontamination. An ion-exchange cycle is included as a tail-end step for additional decontamination of the plutonium and uranium streams.[2] Studies were initiated to explore the feasibility of employing niobium pentoxide as a scavenger to remove residual fission-product activity from the uranium stream. A decontamination factor of 10 resulted from precipitation of approximately $10^{-3}M$ niobium as the pentoxide in a uranium product solution. The precipitate was, however, difficult to separate by either centrifugation or filtration.

An alternative procedure, sorption of activity on solid beds of partially dehydrated niobium pentoxide, also appears effective in removing zirconium and niobium from uranium product solutions. Decontamination performance of a niobium pentoxide bed was better than that of a silica-gel bed. Gross gamma factors of 3 were obtained on niobium pentoxide after 40 bed volumes of throughput as compared to only 2 on silica gel after two bed volumes of throughput.

Modified Purex and Redox Processes

Various modifications of the basic Purex and Redox processes have been developed to handle uranium alloys. In the Darex process stainless-steel–uranium alloys are dissolved in dilute aqua regia. Tributyl phosphate can be used to separate the uranium from chloride ion and from the dissolution products of stainless steel.[2] In tests with 30 per cent TBP and kerosene, 99.9 per cent of the uranium was extracted from the Darex solution. Chloride ion was discharged to the aqueous waste stream. The extraction coefficient for chloride ion was found to be 0.08 (organic/aqueous). A small amount of chloride ion that did extract was easily stripped from the solvent with $0.01M$ HNO_3.

One of the proposed fuels for the Rural Cooperative Reactor would contain, after irradiation, a uranium-plutonium-thorium mixture. Satisfactory recovery of this fuel has been demonstrated with a Thorex type flow sheet, wherein one volume of feed is contacted with two volumes of HNO_3 and four volumes of 30 per cent TBP in kerosene.[3] A more dilute feed solution than is normally used in the Thorex process is employed. The solution was 145 g/liter of thorium and 80 g/liter of uranium in $2M$ HNO_3.

In processing enriched uranium-aluminum alloys, a three-cycle two-solvent operation has proved satisfactory.[4] In the first cycle TBP is used to separate the uranium from aluminum and the bulk of the fission products. The remaining cycles employ a Redox type flow sheet

in which methyl isobutyl ketone is used for the purification of the uranium. In preparing the feed solution for this process, 5.6M HNO_3 is used to dissolve the uranium-aluminum alloy to give a feed solution of 2M HNO_3 and 1M aluminum nitrate. It has also been shown that the second- and third-cycle aqueous waste streams may be returned to the first cycle as a scrub solution,[5] indicating the possibility of improving acid economy and reducing waste-handling problems. The possibility of a build-up of zirconium and plutonium due to the recycle of waste streams was eliminated by adding phosphoric acid to the feed to form unextractable complexes.

Degradation of Process Solvents

Under gamma irradiation TBP breaks down into dibutyl and monobutyl phosphates, phosphoric acid, butyl alcohol, ether, various polymers, and gaseous products of hydrogen and hydrocarbons. The principal degradation product is dibutyl phosphate (DBP). With water-saturated TBP the yield of DBP is lowered by 30 per cent. Studies of irradiation damage to TBP and various diluents showed that in paraffin hydrocarbons the diluent does not affect the yield of DBP. However, benzene lowered and carbon tetrachloride raised the yield.[6]

In most processing schemes TBP is usually diluted with kerosene. It has been found that, in the presence of nitrous acid, kerosene reacts to form degradation products that complex uranium. These were demonstrated to be proportional to the amounts of aromatic and olefinic compounds present in the kerosene. Uranium complexed in the kerosene phase by the degradation products cannot be removed by sodium carbonate or HNO_3 scrubbing.[7]

A new test has been developed to give a quantitative measure of the degree of solvent degradation due to radiation damage. This test employs the treatment of the solvent with zirconium tracer and is called the "zirconium index test." The solvent degradation is determined by the amount of tracer zirconium that cannot be removed from the solvent[8] by scrubbing with 3M HNO_3. This concentration of zirconium is referred to as the "Z" index and is expressed as the number of moles of zirconium retained per billion liters of solvent. Values obtained for the Z index of typical samples[9] of various solvents are shown in Table III-1.

Table III-1 ZIRCONIUM RETENTION OF TYPICAL SOLVENT SAMPLES

Solvent sample	Z index
Virgin	6–10
Warm	6–8
Hot plant	27–60
Discarded hot plant	160
Artificially degraded laboratory*	10–10,000

*Exposed to mixtures of nitrous and nitric acid for four to seven days at 40 to 70°C.

Reactions between zirconium and degraded solvent indicated the existence of three species of complexing agents for zirconium and showed that the rates of formation and decomposition of these complexing agents are slow. Virgin process solvent was degraded in the laboratory at 40°C for five days. Subsequent exposure of the degraded solvent to both NaOH and HNO_3 followed by tests for zirconium retention indicated that each liter of solvent contained about 200×10^{-9} equivalents of acidic complexing agents, 400×10^{-9} equivalents of complexing material that was amphoteric, and 500×10^{-9} equivalents that were neither basic nor acidic.

Quantitative measurements of the rates of formation of DBP and its effects on zirconium extraction were made to provide the basis for accurate definition of the permissible residence time of solvent per cycle through the extraction portion of the process.[10] The results showed that residence times as long as 4 hr can be tolerated at 60°C and as long as 15 min at 80°C. The DBP formation rate in the organic phase alone increases with temperature and with concentration of HNO_3, e.g., rates at 70°C are generally a factor of 20 greater than those at 40°C. The effect of radiation on the rate of DBP formation was measured. Thirty per cent TBP and dodecane containing 0.82M HNO_3 was exposed to 10^7 r of gamma irradiation within a period of 48 hr. The irradiated sample contained 0.06 per cent DBP. No detectable DBP was formed in a control test in the absence of irradiation. Preliminary measurements indicated that the effect of uranium is larger than that of equivalent molar quantities of HNO_3 in accelerating DBP formation rates. Results also indicated that the aqueous uranium phase has a greater influence in accelerating the rate of DBP formation than does the aqueous acid phase. In order to establish the effect of DBP on the performance of solvent in the Purex process, the effect of its

addition to 30 per cent TBP–ultracene on the distribution coefficient of zirconium between $3M$ HNO_3 and solvent was studied. It was found that at 23°C, as little as 0.001 vol. % DBP in the solvent makes a measurable contribution to the zirconium distribution coefficient.

A new hypothesis has been advanced which indicates that retention of fission-product activity in the solvent may not be solely due to complexing with degradation products. It is hypothesized that colloidal particles in the aqueous feed absorb certain fission-product activities, zirconium, niobium, and ruthenium, in particular. These colloidal materials then pass into the organic phase and are retained. Furthermore, the colloidal particles are not removed in subsequent stripping operations nor in the solvent cleanup scrubbing step. Thus the solvent becomes radioactive, and, on reuse, the slow desorption of the fission-product activity on the colloidal particles then serves to limit the attainable over-all decontamination factor for the process. Experimental proof was provided which substantiated this hypothesis.

Studies of Amine Extractants

Amines have been found to act essentially as liquid anion-exchange resins that can be loaded in high acid and eluted in water or dilute acid. A systematic study of amines as uranium extractants is in progress. Data have been obtained for uranium extraction with trioctylamine in a kerosene-alcohol diluent. Long-chain alcohols are used as modifiers to increase the solubility of amine salts in the diluent. The modifiers cause some loss in uranium extraction power.[11]

Neptunium(IV) and plutonium(IV) form anionic nitrate complexes at high HNO_3 concentrations which are readily extractable by tertiary amines. Tests of 10 per cent trioctylamine in xylene showed that the best extraction results were obtained in $4M$ to $6M$ HNO_3 solutions. Stripping was satisfactorily accomplished with water. An irradiation dose of 44 watt-hr/liter did not alter appreciably the extractant characteristics of the amine.[12]

Trioctylamine has been demonstrated as a satisfactory extractant for Pu(IV) from high burn-up reactor fuels.[13] Good decontamination factors were obtained, and the radiation resistance of the solvent was found to be satisfactory. Xylene was used as the diluent for the amine. Several alternate diluents were tested. In many cases two organic phases formed when in contact with $2M$ HNO_3 solutions containing uranium. Nitric acid was needed in the aqueous phase to prevent the precipitation of plutonium at the interface. Extraction coefficients were reported for a number of tertiary amines in the series of tripropylamine through trioctylamine. Extraction power was best with the higher amines. The highest extraction coefficient, E_a^o of 310, was obtained with triisoöctylamine. With all extractants studied, beta and gamma activities which extracted were difficult to remove by scrubbing.

Triisoöctylamine in HCl systems can be used to separate uranium from thorium.[14] Uranium, but not thorium, forms an anionic complex in HCl. It was possible to strip uranium from the amine with water, $0.1M$ HCl, or $0.1M$ HNO_3. Rare earths were not extracted, and zirconium extraction was low. Niobium extraction was low in dilute acids, and ruthenium was found to be somewhat extractable. Using potassium dichromate as a holding oxidant, it was possible to extract Pu(VI) from $5M$ HCl solutions. Plutonium(III) did not extract. Triethylenetetramine gave an improved ruthenium decontamination factor greater by a factor of 1.6, total beta decontamination factor by a factor of 4, and total gamma decontamination factor by a factor of 5 using Purex HNO_3 conditions. Under Redox conditions where dichromate is present, a precipitate formed.[15]

Amines show promise for the extraction of uranium from ore leach liquors. For processing with the TBP extractant, the tolerance limits given in Table III-2 have been placed on ore concentrates by the National Lead Co. of Ohio.[7] Tests have shown that by using trilaurylamine it may be possible to relax some of the tolerance limits. The use of trilaurylamine was successfully demonstrated for the economical recovery of uranium from Lakeview leach liquor.[16] Conventional TBP processing of Lakeview leach liquor is difficult because of the high molybdenum content of the liquor. The extractant used was 5 per cent trilaurylamine in a diluent of 8 per cent decyl alcohol in kerosene. The high molybdenum concentration caused no difficulty. In tests of other tertiary amines, molybdenum precipitated in the diluents; in tests of secondary amines, the precipitate appeared in the strip solution.

Table III-2 TOLERANCE LIMITS FOR NATIONAL LEAD CO. OF OHIO REFINERY FEED MATERIALS[7]

Constituent	Tolerance limits	Effect of deviation beyond limits
Uranium	30% (min.) of feed material (as received)	Reduces plant capacity
Sulfate	40% (max.) on U basis	Reduces extractability of U from feed slurry
Calcium sulfate	(% Ca × % SO_4), 40 on a U basis	Causes column scaling
Phosphate	7% (max.) on a U basis	Reduces extractability of U from feed slurry
Phosphate–sulfate	(5 × % PO_4 + % SO_4), 35 on a U basis	Reduces extractability of U from feed slurry
Chlorides	0.125% (max.) on a U basis	Corrosion
Fluorides	0.125% (max.) on a U basis	Corrosion
Iron	40% (max.) on a U basis	Reduces product purity
Vanadium	5% (max.) on a U basis	Reduces product purity
Boron	0.7% (max.) on a U basis	Reduces product purity
Copper	4% (max.) on a U basis	Reduces product purity
Organic material	0.12% (max.) on a U basis	Possible explosion hazard with HNO_3; reduced extractability due to addition of surfactants
Arsenic	Unknown (feed containing 7% As on a U basis has been processed satisfactorily)	Reduces product purity
Molybdenum	Unknown (feed containing 1.5% Mo on a U basis has been processed satisfactorily)	Reduces product purity
Thorium (no phosphate)	350 ppm (max.) on a U basis	Reduces product purity
Thorium (plus phosphate)	20,000 ppm (max.) on a U basis with 15% PO_4 present on a U basis	Reduces product purity
Rare earths, cadmium, lead, zinc, chromium, zirconium, titanium	Data on which to base limiting concentrations of these elements in feed materials are not yet available	Reduces product purity

Equipment Development

A horizontal mixer-settler with a vertical dimension small enough to avoid nuclear reaction at concentrations of fissionable material up to 400 g/liter has been operated successfully at Savannah River at total flows of 4 gal/min on a TBP-kerosene organic phase and an HNO_3–aluminum nitrate aqueous phase. Uranium transfer efficiencies greater than 80 per cent were obtained.[17] Two sizes of continuous solvent washers have been developed for the removal of fission products from the TBP-kerosene solvent. The first, in the form of a 10-ft-diameter tank, has been used to wash a 20 gal/min flow of solvent with sodium carbonate solution to give gross gamma decontamination factors of 5 to 10. The ratio of solvent to wash volumes is 100. The second washer is in the form of a 7-in. pipe to avoid nuclear reactions that might occur from the build-up of fissionable materials in the wash. This has a processing capacity of 0.5 gal/min for TBP-kerosene solvents.

Operating characteristics and detailed design information are given for 17 steam jet syphons that have been operated on radioactive aqueous solutions and TBP. Controllable rate jets have been operated with a flow accuracy of ±2 per cent over the range from 1 to 27 gal/min. Constant-rate jets with flows from 15 to 100 gal/min have operated with suction lifts as high as 14 ft of water and discharge heads as high as 90 ft of water.

Criticality Studies

In processing alloys containing fissile materials, consideration must be given to problems of nuclear safety. Some factors that play an important role are the relative amounts of moderating elements and fissionable material

present and the size and shape of the enclosed volume.

A compilation of empirical formulas is available for estimating the critical volume of various shapes for aqueous solutions of U^{235}. Very good agreement was obtained between calculated and experimental volumes over a wide range of variables.[18]

Ketzlach has prepared a survey of the application of the principles of nuclear safety to the sequence of operations employed in processing spent nuclear fuels. Representative curves are presented, giving the critical dimensions for both the solid-state and acid solutions[19] of systems containing U^{235} or Pu^{239}. In another publication Ketzlach has summarized the criticality data for plutonium. Data are given for the critical volume of various shapes for plutonium metal and for HNO_3 solutions. Data are also presented to show the effect of reflectors and Pu^{240} content on the critical volume.[20]

Ion-exchange Processes

During the past quarter considerable work has been done on the application of ion exchange to atomic energy problems. The current status of ion-exchange research has been reviewed by Kraus and Nelson.[21]

The distribution coefficients of thorium and praseodymium between Dowex-1 and aqueous HNO_3 have been determined.[22] Separations between thorium and the rare-earth elements, samarium, lanthanum, neodymium, europium, yttrium, and cerium, were also obtained. The distribution coefficients (grams radioelement per gram dry resin/grams radioelement per milliliter of solution) increased with increasing HNO_3 molarity up to 7*M* HNO_3 and then decreased with further increase in HNO_3 molarity. Maximum values were 300 for Th(IV) and 20 for Pr(III). Complete separations of all rare-earth metals (except cerium) from thorium were achieved by elution of the resin column with 5*M* to 8*M* HNO_3.

Separation of niobium from zirconium by a cation exchanger has been demonstrated.[23] The process involves absorption of carrier-free Zr^{95} and carrier-free Nb^{95} from 0.1*N* HCl onto a cation resin column (Dowex-50W-X8, 200 to 400 mesh), followed by elution with 0.1*N* HCl containing 0.3 per cent hydrogen peroxide until the niobium has been removed. Zirconium is then stripped from the column using 0.5 per cent oxalic acid.

The pressure drop and flow characteristics of the anion-exchange resin (Amberlite IRA-401, 20 to 50 mesh) were investigated in a moving-bed ion-exchange contactor.[24] In a water system with a combined feed and scrub flow of 3.0 liters/min, a 4-in. resin push (6-in. water push) was obtained with an air pressure of 10 psig. In an acid system (~6.5*M* HNO_3) with the same flow, however, an air pressure of 30 psig was necessary to obtain a 1-in. resin push with a 6-in. water push.

Pressure drop and flow characteristics of the anion-exchange resins (Dowex-1-4X, 50 to 100 mesh, and Permutit SK, 20 to 50 mesh) were investigated in a moving-bed ion-exchange contactor.[25] Dowex-1 resin failed to push at aqueous feed rates commensurate with the plant capacity. The Permutit SK resin pushed with relative ease at the maximum projecting feed rates, exhibiting characteristics essentially identical to those for Amberlite IRA-401 20- to 50-mesh resin.

For all resins studied to date,[24] the concentration of plutonium absorbed on the resin increases approximately linearly with the logarithm of time with the exception of 1 per cent cross-linked Dowex-1. The Dowex-1-X-1 loads much more rapidly than the other resins, and the plutonium concentration varies in a more complicated fashion with time. The greater shrinkage that this resin undergoes on loading may account in part for its more complicated rate behavior as compared with higher cross-linked resins.

1. *Recovery of Plutonium from Purex Waste.* A series of runs are in progress to determine the plutonium absorption characteristics of Dowex-21K and Amberlite IRA-401 resins for feeds of the plutonium level expected in Purex waste. With synthetic first-cycle aqueous waste spiked to 50 mg plutonium per liter, Amberlite IRA-401 (20 to 50 mesh) exhibited a plutonium capacity (to 50 per cent breakthrough) of 10, 10, and 15 g plutonium per liter of resin at temperatures of 60, 40, and 25°C, respectively.

Recent laboratory studies[26] that showed acceptable absorption rates (corresponding to a column capacity of 66 g plutonium per liter resin at 50 per cent breakthrough) for Permutit SK at 60°C, excellent elution rates at temperatures of 40°C and higher, and chemical stability

at least as good as for other 20- to 50-mesh resins led to the selection of Permutit SK for the Purex concentration steps.

Column runs with Amberlite IRA-401 and Dowex-21K at 25°C with synthetic Purex waste showed capacities at 10 per cent breakthrough (corresponding to recovery of greater than 95 per cent of the feed plutonium) of 0.5 and 1.8 g plutonium per liter resin for Amberlite IRA-401 at feed concentrations of 2 and 10 mg plutonium per liter, and 10 g plutonium per liter resin for Dowex-21K at 56 mg plutonium per liter feed. Although low, these capacities are adequate to make application of this process to Purex waste economically attractive, particularly since the installation of an anion-exchange unit will provide a separate rework facility for off-standard wastes.

2. *Processing of PRP Fuels.* The recovery of plutonium from Plutonium Recycle Project (PRP) feeds by anion exchange requires the use of about 7*M* HNO_3 and a uranium concentration[24] less than 180 g/liter. Feed preparation could best be made by dissolving to this acidity rather than dissolving to low acidity and diluting with acid. An anion-exchange run was made in the laboratory to determine what effect this dissolving procedure might have on fission-product decontamination. Irradiated uranium was dissolved to a terminal acidity of 8*M* HNO_3. This solution was diluted to 10 per cent level with cold feed and was filtered prior to being fed to the column. The loading out of 8.0*M* HNO_3, 103 g/liter uranium, 0.46 g/liter Pu(IV), 2.7×10^9 counts/(min)(ml) zirconium-niobium, 1.4×10^8 counts/(min)(ml) ruthenium-rhodium, washing with 7.5*M* HNO_3, and elution with 0.35*M* HNO_3 were all conducted at 55°C. The loaded resin was washed with 60 column volumes of wash, and the plutonium was then eluted at a concentration of ~ 19 g/liter. Decontamination factors were 6.4×10^4 for gross gamma, 2.3×10^6 for zirconium, and 2.8×10^4 for niobium. The limiting fission product was niobium, which accounted for about 99 per cent of the gamma activity in the product.

The gross gamma decontamination obtained in this run is about threefold greater than that obtained in an earlier run that employed feed prepared from Purex dissolver solution. It is not known whether this improvement was due to the modified dissolving procedure or perhaps to a lower solids content in the laboratory-prepared dissolver solution. In any event it appears that dissolving to a high terminal acidity will certainly not impair fission-product decontamination.

3. *Head-end Treatment.* Uranium carbonate solution containing cesium spiked with Cs^{137} tracer was passed through a cation-exchange column.[27] Analytical results showed 93 per cent uranium recovery.

An experiment was carried out in which zirconium was complexed with an excess of ammonium carbonate, and the solution containing a small amount of cesium spiked with Cs^{137} was passed through a 15-in. column of an inorganic cation exchanger from the Minnesota Mining & Manufacturing Co. The total weight of the exchange material was about 80 g. The total equivalents were 1.24 for NH_4^+ and 0.087 for zirconium. About two-thirds of the zirconium solution passed through the column before any cesium broke through. Upon passing the whole zirconium solution through the column and washing with distilled water until no activity was present in the effluent, the total amount of cesium remaining on the column was 92 per cent. Later data showed that 0.52 equivalent of zirconium can be complexed in the presence of 1.24 equivalents of NH_4^+. This will permit greater zirconium concentrations, with no increased cation concentration, and greater separation of cesium from zirconium.

Precipitation Processes

Work done at Idaho on the separation of kilocurie quantities of Ba^{140} from spent Materials Testing Reactor (MTR) fuel elements is reported on pp. 28 to 34.

Volatility Processes

Interest continues in fluoride volatility processes, i.e., processes in which fluorination is used to convert uranium to uranium hexafluoride and decontamination is subsequently effected by distillation or by absorption-desorption.

Fused-salt Processes

One of the possible fluoride volatility process variations is directed at the dissolution and decontamination of zirconium-uranium alloy fuels.

The alloy is dissolved by hydrofluorination in a mixture of molten fluoride salts (sodium fluoride–zirconium fluoride) at 600°C. The uranium is recovered as the hexafluoride with a subsequent fluorine sparge.

Pilot-plant studies of a dissolver-hydrofluorinator are under way. Examination of an "A" nickel vessel used in preliminary work was made, and substantial corrosion was found.[28] In an effort to avoid corrosion problems during the hydrofluorination step, a graphite cold-wall dissolver was designed and given preliminary tests by Horizons, Inc. Installation of this unit with some modifications has begun at ANL.[29]

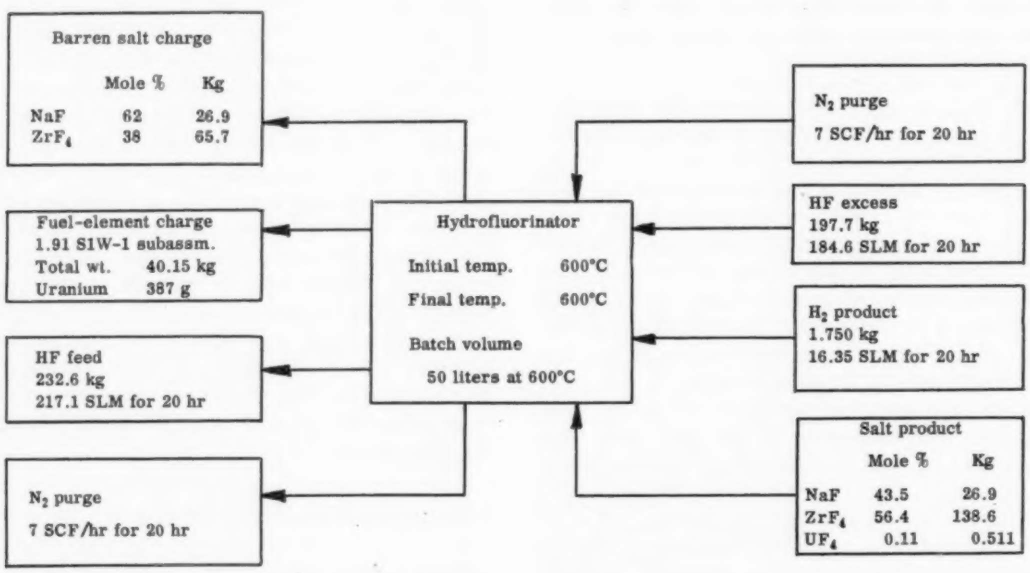


Figure 1—Process materials and flows for NaF-ZrF_4 system. Data obtained from Ref. 31, p. 6.

A pilot-plant facility for the dissolution of zirconium-uranium fuel alloys also has been recently installed at ORNL.[30,31] A flow diagram of the proposed process is shown in Fig. 1. Two salt mixtures are being studied, sodium fluoride–zirconium fluoride and sodium fluoride–lithium fluoride. The temperature of operation will be between 600 and 700°C.

Some time ago a circulating fuel reactor using a molten mixture of fluorides as the fluid fuel was developed at Oak Ridge. This was called the Aircraft Reactor Experiment (ARE). It was operated at various power levels up to 2.5 Mw. The fuel mixture consisted of 53.1 mole % sodium fluoride, 40.7 mole % zirconium fluoride, and 6.2 mole % uranium tetrafluoride. The total amount of U^{235} added to the system to achieve criticality was approximately 135 lb. This reactor has been described in detail in the literature.[32–35]

After irradiation this fuel was very similar to the fused-fluoride mixture produced by the dissolution of irradiated zirconium-uranium fuel alloy in fused sodium fluoride–zirconium fluoride.[36] It was natural, therefore, to consider recovering the uranium from this fuel by techniques similar to those previously considered for the zirconium-uranium alloys. The processing was carried out in the fluoride volatility pilot plant at Oak Ridge.[37] It consisted of sparging fluorine gas through the molten salt at 650°C to volatilize the uranium as the hexafluoride, followed by absorption of the uranium hexafluoride on solid sodium fluoride beds at 100°C, and desorption in a stream of fluorine at a temperature of 400°C. Laboratory data have indicated that this procedure should give beta-gamma decontamination factors in excess of 10^6 for the entire process. Operating data on the process runs are not yet available.

In seven shakedown runs prior to the processing of the ARE fuel, slightly over 84 per cent of the uranium was recovered in the product re-

ceivers. Nonrecoverable losses were 0.03 per cent. Material balance[30] was 95 per cent.

Laboratory studies on the absorption and desorption of uranium hexafluoride on sodium fluoride beds indicated that (1) for the same length, larger diameter beds were more effective, (2) uranium recovery was much lower using nitrogen rather than fluorine for the sweep gas during the desorption, (3) the formation of a nonvolatile uranium complex during the adsorption increased with temperature up to 450°C, and (4) decontamination was better if the sodium fluoride was in finer particles, although plugging difficulties increased with decrease in particle size.[30,38,39]

In laboratory fused-salt equilibrations, less than 50 ppm uranium was found to remain with the equimolar sodium fluoride–zirconium fluoride salt at 600°C after contact with fluorine and uranium hexafluoride gas mixtures[40] up to a uranium hexafluoride partial pressure of 250 mm Hg.

Process Chemistry of Fluoride Systems

Tabular values of the saturated vapor pressure of liquid uranium hexafluoride and the derivative of the vapor pressure with respect to uranium hexafluoride concentration have been published.[41] This is a convenient form of data based on experimental work published earlier.[42]

There is interest in the fluoride chemistry of plutonium as well as uranium, since reactions involving the fluorination of plutonium to the tetrafluoride, followed by its conversion to the hexafluoride with elemental fluorine, may provide a basis for the recovery of decontaminated plutonium from spent reactor fuels by an all-volatility process. Data on the fluorination rates of plutonium tetrafluoride have been presented previously in terms of a diminishing sphere correlation.[43] More recent data[28] and a reconsideration of the diminishing sphere treatment have shown that the reaction can be represented better by the following rate equation:

$$X = Kf(P)St\ e^{-\Delta E/RT}$$

where X is the amount of plutonium tetrafluoride reacted in milligrams per square centimeter per hour, f(P) is an unknown function of the partial pressure of fluorine and is equal to unity for 1 atm of fluorine pressure, S is the exposed surface area of the sample in square centimeters, t is time in hours, ΔE is the activation energy in calories per mole, R is the gas constant in calories per degree per mole, and T is the absolute temperature in degrees Kelvin. The values of K and ΔE for plutonium tetrafluoride from three sources are indicated in the following table.

Source of PuF_4	K	ΔE, cal/mole
A	9.17×10^5	−12,500
B	7.06×10^5	−11,700
Dissolution residue	11.7×10^5	−10,400

The plutonium tetrafluoride from sources A and B had been prepared by high-temperature hydrofluorination procedures. That listed as dissolution residue was prepared by the dissolution of uranium-plutonium alloys in liquid bromine trifluoride. This material was very finely divided.

Attempts to determine the nature of the fluorine pressure term in the general equation suggested that the pressure effect is a function of both the fluorine pressure and the temperature. Experiments were performed with fluorine partial pressures of 0.25, 0.33, 0.50, 0.75, and 1 atm at temperatures of 200, 300, and 375°C. The reaction rate reached a maximum at 0.75 atm pressure at all three temperatures, but the effect diminished as the temperature was increased. No attempt has been made to explain this effect in terms of the reaction mechanism.

Phase diagrams[44] are available for the systems LiF-BeF_2, NaF-BeF_2, NaF-LiF-BeF_2, and LiF-BeF_2-UF_4. The binary system BeF_2-UF_4 shows no intermediate compounds and has a eutectic at a concentration of about 1 mole % UF_4 and 530°C. Systems containing ThF_4 are being actively investigated. Virtually complete phase diagrams are presented for BeF_2-ThF_4, LiF-ThF_4, and NaF-ThF_4 systems. Because PuF_3 is believed to be less oxidizing and therefore less corrosive than PuF_4, the solubility of the former was examined as a potential reactor fuel. The solubility in a particular salt, NaF-BeF_2 (57 to 43 mole %), of low melting point (360°C) is given in Table III-3.

The solubilities of the noble gases in molten sodium fluoride–zirconium fluoride (53 to 47 mole %) obey Henry's Law, i.e., they increase with increasing temperature, decrease with increasing atomic radii, and are not appreciably affected by the presence of 10 wt.% uranium

tetrafluoride. The behavior of hydrogen fluoride is different: its solubility decreases with

Table III-3 SOLUBILITY OF PuF_3 IN NaF-BeF_2 (57 to 43 MOLE %)

Temp., °C	Filtrate analysis	
	Pu, wt.%	PuF_3, mole %
538	1.10	0.20
600	1.32	0.25
652	2.16	0.41

temperatures. Reported in Table III-4 are the Henry's Law constants and heats of solution of six gases in the above salt at 600°C.

Table III-4 SOLUBILITY PARAMETERS FOR GASES IN MOLTEN SALT*

Gas	Solubility constant, $\frac{\text{(g-moles gas)}}{(\text{cm}^3 \text{ salt})(\text{atm})}$	Heat of solution, kcal/mole
Helium	21.6×10^{-8}	6.2
Neon	11.3×10^{-8}	6.0
Argon	5.1×10^{-8}	6.2
Xenon	1.9×10^{-8}	11.1
Krypton	$3 \pm 1 \times 10^{-8}$†	9.5 ± 1.5†
HF	1.23×10^{-5}	−4.5

*Composition: 53 mole % NaF, 47 mole % ZrF_4.
†Estimated.

The rare-earth trifluorides are sparingly soluble in NaF-ZrF_4 (53 to 47 mole %) mixtures.[44] In this solvent the solubility of CeF_3 is 2.3 mole % at 600°C and 4.3 mole % at 800°C.

Table III-5 COMPARISON OF SOLUBILITY OF CeF_3

Temp., °C	Solubility, mole % CeF_3	
	In NaF-ZrF_4*	In NaF-BeF_2*
750	3.2	1.1
700	2.7	0.65
600	1.9	0.29
550	1.7	0.17

*53 to 47 mole %.[44]

Preliminary experiments on the solubility of CeF_3 in NaF-BeF_2 (57 to 43 mole %) have also been made. A comparison of data from the two salts is given in Table III-5.

Pyrometallurgical Processing

Pyrometallurgical processes give promise of reducing processing costs because of the elimination of chemical conversions and of their ability to process short-cooled fuel. Their development has been encouraged by and has paralleled the development of high-performance reactors. Low processing costs are particularly important for these reactors because of the high fissionable material content. Because of this factor processing must be accomplished as quickly as possible to keep inventory charges to a minimum; because a large number of cycles are required for complete fuel consumption, processing costs must be kept to a minimum.

Pyrometallurgical processes are not generally high decontamination processes; therefore completely remote fuel processing and refabrication are required. The processing accomplishes only the requisite decontamination for repair of irradiation damage and the replenishment of the fissionable material content.

Melt-refining Studies

As described in the previous Reviews, the melt-refining process consists simply in melting the fuel in a zirconia crucible and holding it molten for several hours at an elevated temperature (1300 to 1400°C). Considerable fission-product removal is realized through volatilization and drossing reactions.

In anticipation of the use of plutonium fuels in the Experimental Breeder Reactor (EBR-II), experiments have been made using a 20 per cent plutonium alloy to ascertain the behavior of plutonium in the melt-refining process.[29] Plutonium remained with the bulk metal as desired. A slight plutonium enrichment in the skull was indicated, but plutonium recovery would be essentially comparable to that of uranium.

The behavior of several fission products not previously investigated has been followed in tracer-scale experiments using fissium (a uranium alloy containing noble metals in the following percentages: molybdenum, 3.4; ruthenium, 2.6; rhodium, 0.5; and palladium, 0.3). Such tracer-scale experiments are valuable in providing indications of whether or not an element is removed from the bulk metal; however, the mechanism of removal, the rate of removal, and the ultimate fate of an element (e.g., percentage volatilized vs. that retained in slag

layers) are strongly dependent on concentration. The recently studied fission products are technetium, neodymium, europium, barium, cadmium, iodine, bromine, and xenon.[29] Technetium behaved as a noble metal with no partition between bulk metal and slag phases. Essentially complete removal of the rare-earth metals (lanthanum, cerium, and neodymium) was effected in the presence of large concentrations of cerium (0.6 wt. % initially). Europium was less completely removed than were the other rare earths (90 vs. 99 per cent). Xenon, although removed fairly well from bulk metal, was retained in the dross. A similar experience was previously encountered with cesium. In tracer-level tests appreciable cesium (50 per cent) was retained in the skull, but removal was essentially quantitative from material irradiated to 0.4 per cent burn-up. Complete barium and strontium removal was effected by preferential oxidation and incorporation into the skull. Cadmium is unstable, and volatilization appears to be the important factor in its removal. Iodine was fairly completely removed from the bulk metal, but a large fraction was retained in the skull. About one-half the bromine was retained in the bulk metal. The rate of removal of these elements may be dependent upon the stabilities of the uranium halides at the furnace pressures employed.

Pilot Applications of Melt Refining

Two pilot plants are being designed in which the melt-refining process will be used, one at ANL for processing fuel from the EBR-II fast breeder reactor and the other at Atomics International in California.

A fully integrated fuel cycle (fuel processing, refabrication, and return of fuel to the reactor) will be demonstrated in the EBR-II reactor complex. The progress of this project was reflected by the presentation of two papers[45,46] at the Sixth Hot Laboratories and Equipment Conference held in Chicago in March 1957. The design of the plant and equipment for high-temperature processing of the spent EBR-II reactor fuel was described. A dominating and unique feature of this processing plant is a large 62-ft-I.D. 21-ft-high heavily shielded circular processing cell that will contain equipment for the complete processing and refabrication of fuel elements. The cell atmosphere will be purified argon. Figure 2 is a view of a model of this plant, and Figs. 3 and 4 are plan and section views.

The present schedule calls for construction of the processing plant to begin in the first quarter of 1959. Detailed drawings are being prepared by an architect-engineer. Design of a laboratory and service building is complete, and construction bids are now being sought.

Molten Metal Extraction

The partition of plutonium between an immiscible molten metal extractant and uranium alloy systems is the basis of several extraction processes for separation of plutonium from uranium. A particularly important application is the recovery of plutonium bred in uranium blankets.

A magnesium extraction process is being developed for recovery of plutonium bred in the blanket of the EBR-II reactor.[47] In order to allow operation below the boiling point of magnesium (1106°C), a uranium–5 wt.% chromium eutectic alloy has been employed as the blanket material. After extraction of the plutonium, the magnesium is volatilized to effect a plutonium-magnesium separation.

The use of graphite as a container material for the extraction resulted in excessive losses of plutonium by carbide drossing. Tantalum is currently being evaluated.

Measurements of the chromium distribution coefficient show the extraction of about 0.15 wt.% chromium into magnesium at 950°C. The solubility of chromium drops to about 0.02 wt.% on cooling to 675°C. Knowledge of the chromium behavior is important in order to determine the magnitude of the problem created by the presence of some chromium in the plutonium product.

Silver is also being investigated as an extractant metal. Distribution of plutonium between liquid uranium and silver phases was measured for a 0.2 per cent plutonium alloy. Extraction coefficients[48] at 1225°C were found to be between 20 and 30. The behavior of cerium in the silver extraction process has been investigated.[49] Distribution coefficients are highly in favor of silver. Cerium may be removed from the silver by oxidative drossing or by extraction using salt mixtures such as sodium chloride–silver chloride.

Several processes are under development which involve dissolution of fuel or fertile ma-

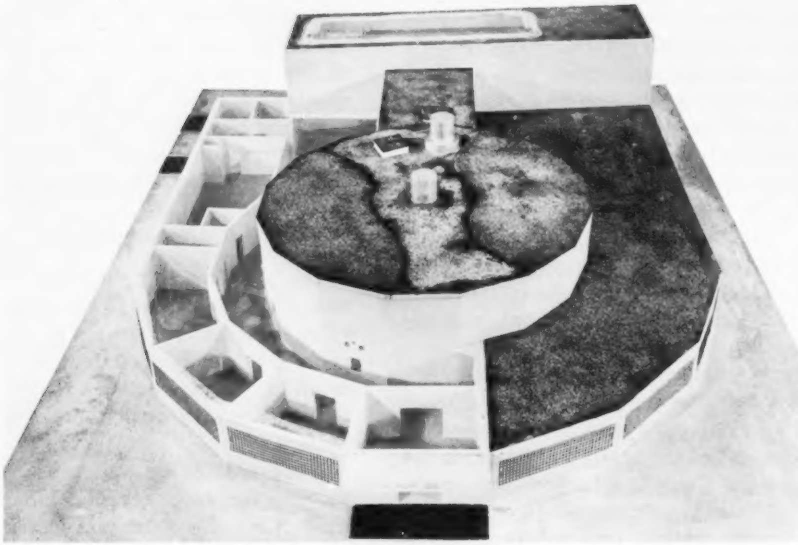


Figure 2 — EBR-II processing building, exterior. Data obtained from Ref. 45.

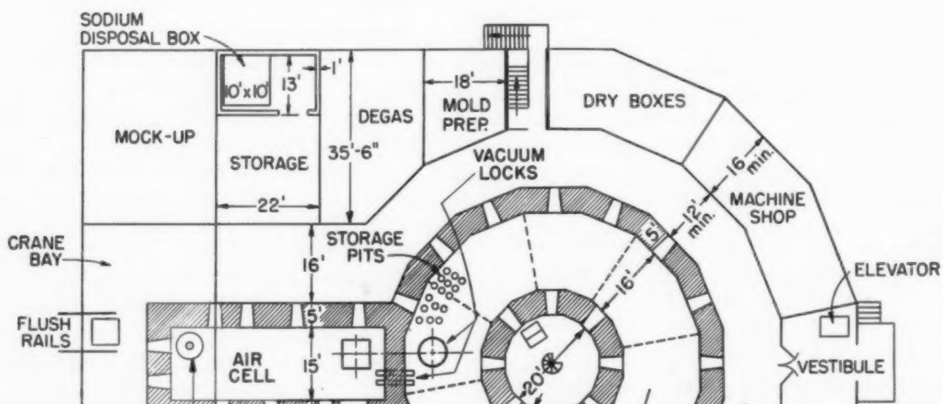


Figure 3 — EBR-II processing building, main floor. Data obtained from Ref. 45.

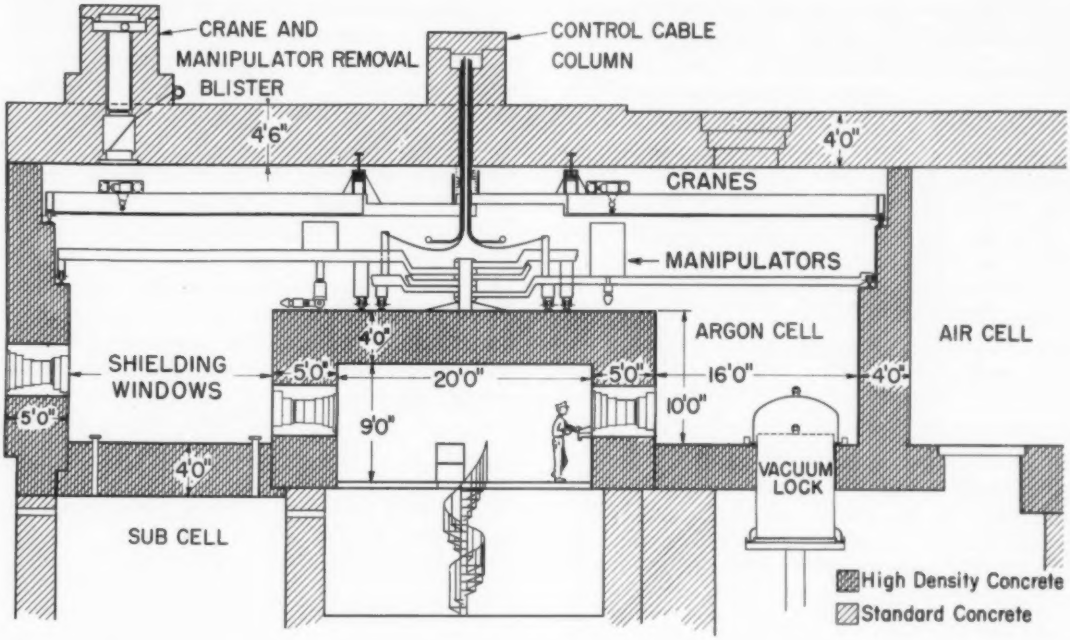


Figure 4—Argon cell, section view. Data obtained from Ref. 45.

terial in a metal solvent and fractional crystallization of an intermetallic compound therefrom. These processes have been described in the previous Reviews. A survey by Isserow of metal solubilities in several liquid-metal systems was recently reported.[50]

Processing of Plutonium-rich Fuels

The investigation of pyrometallurgical methods for the purification of plutonium-rich fuels is under way at Los Alamos Scientific Laboratory (LASL).[51] Results have been reported for three oxide-slagging runs made at a temperature of 1400°C in a magnesium crucible. Excellent removal of rare earths and about 75 per cent removal of zirconium were realized after 5 hr at 1400°C. The over-all product yield (shown in Table III-6) varied between 84 and 89 per cent. The low yields are believed to be due in part to the fact that the melt was poured at 1000°C.

Four liquation experiments were conducted wherein fissium alloy (this alloy had the following approximate weight per cent composition: plutonium, 91; iron, 2.5; zirconium, 1.0; molybdenum, 1.0; ruthenium, 1.4; lanthanum, 1.8; and cerium, 1.3) was held in the molten state at 500°C in a crucible and sampled periodically by filtering at temperature. Typical results obtained at 500°C are shown in Table III-7. It was possible to remove most of the zirconium,

Table III-6 SUMMARY OF CONSECUTIVE OXIDE SLAGGING RUNS AT 1-KG SCALE[51]

	Element in alloy, wt. %			
Element	Before processing	After Run II-1*	After Run II-2*	After Run II-3*
Pu	89.3	89.6	92.3	92.6
Fe	2.47	2.52	2.59	2.74
Zr		0.8	0.6	0.28
Mo	0.78	0.82	0.87	0.91
Ru	1.22	0.80	1.29	1.36
Ce	1.14	0.75	0.49	0.02
La	1.77	0.57	0.11	0.09
Mg				0.02
C				82†
O				10†
Pu yield, %		88.5	85.7	84.2

*Run II-1: 120 min at 1400°C; Run II-2: 80 min at 1400°C; and Run II-3: 120 min at 1400°C.

†Parts per million.

Table III-7 TYPICAL FISSION-PRODUCT SOLUBILITIES[51] AT 550°C IN PLUTONIUM FUEL OF INDICATED COMPOSITION

Element	Initial, wt. %	C/C_0 after liquation* 44 hr	259 hr
Pu	89.2	1.06	1.03
Fe	2.22	0.91	1.07
Zr	0.88	0.025	0.011
Mo	0.78	0.22	0.013
Ru	1.32	0.97	0.80
La	1.79	0.16	0.12
Ce	0.93	0.90	0.68

*C/C_0 = concentration of element relative to initial concentration.

molybdenum, and lanthanum by the simple method of liquation and filtration. However, the times required are excessive. Large-scale experiments will be conducted to determine yield and purification obtained by filtering a large charge.

Also at Los Alamos, solubility of plutonium in mercury has been determined for various temperatures.[51] During cooling from 345 to 20°C plutonium solubility decreases significantly, indicating that a mercury extraction process might be feasible provided that fission-product solubilities are favorable. It is planned to measure the solubilities of individual fission-product elements as a function of temperature.

Processing of Oxide Fuels

Investigation of methods for processing uranium oxide fuels has begun at Atomics International.[52] Size reduction of sintered uranium oxide pellets has been effected by oxygen-hydrogen cycles at 700 to 1000°C. Treatment of irradiated uranium dioxide powder with hydrogen chloride gas at 1300°C resulted in considerable decontamination of ruthenium, tellurium, cesium, and strontium. Rare earths were not significantly removed.

A program has also been initiated at Hanford Atomic Products Operation (HAPO) to devise and test pyrochemical methods for oxide fuels.[24–26] It has been shown that dissolution of uranium dioxide in $KAlCl_4$ is possible. The uranium reaction product is UO_2Cl_2. This may be subsequently dissolved in water, leaving the insoluble aluminum oxide behind, or, by the addition of aluminum, the uranium may be reduced to give a uranium-aluminum alloy.

Container Materials

High-integrity container materials are of great importance in pyrometallurgical processing, and the choice of materials is limited. Container materials are being tested and developed at Ames, Iowa, for potential liquid-metal reactor fuels, metals, and coolants.[53] Preliminary testing of yttrium metal as a container for various molten fuel alloys is being done. An yttrium crucible examined by radiographic means showed no attack by a uranium-chromium eutectic alloy after 1000 hr exposure at 925°C. Experiments are under way on the protection of yttrium from atmospheric attack by chrome plating and by flame spraying chromium. Samples of chrome-plated yttrium have not oxidized in 150 hr in air at 1000°C. Alternatively, chrome stainless steel appears to be a satisfactory backup metal for yttrium. Nickel cannot be tolerated as a backup metal because, even in very small concentrations, it interacts with yttrium.

A borided tantalum crucible has held molten uranium at 1250°C for 7 hr without visible signs of corrosion; however, the resulting ingot contained 550 ppm of boron. Tests are under way to determine whether this is due to a removal excess of boron on the surface.[29]

Powell[54] has investigated niobium-uranium alloys for containing molten uranium eutectic alloys. A protective oxide film was first formed at 400°C. The useful range for a uranium-chromium eutectic was from the melting point 860 to 950°C. Thermal cycling hastened breakdown of the oxide film.

Homogeneous Reactor Processing

Homogeneous reactors are being studied at several sites, principally at Oak Ridge, aqueous, and at Brookhaven National Laboratory (BNL), liquid metal fueled. A potential advantage of homogeneous reactors is that a side stream of fuel can be continuously or periodically withdrawn and processed to reduce the fission-product poisons to some stable and predetermined level. The efficiency of processes developed for this purpose need not be high.

Aqueous Homogeneous Reactors

At Oak Ridge a chemical processing plant is installed as an integral part of the Homogeneous Reactor Test (HRT).[55,56] Preparations were made for active runs in this chemical plant. Studies were continued on the removal of gaseous fission products and iodine from the reactor off-gases and on the behavior of solids expected to be present (corrosion products in fuel solution and corrosion products plus plutonium oxide in the uranyl sulfate blanket solution).

The HRT is designed in such a manner that it is possible to maintain it and replace some equipment items under water. The cell containing the plant was recently flooded, and four items of equipment were replaced: the dissolver, circulating pump, high-pressure heater, and a low-pressure valve.

Separations of solids in the chemical processing loop are made by use of a hydroclone. The hydroclone loop was operated for 300 hr during October. Several leaking valves causing fuel loss were replaced.

Columbia grade G charcoal and several inorganic materials are being studied to determine their adsorption characteristics for xenon and krypton. Several tests have been made on charcoal beds using Kr^{85} in oxygen at 16 to 19°C. A pulse of krypton is injected into the flowing oxygen at the entrance to the bed, and the effluent is monitored with a G-M tube. In a typical bed charged with 520 lb of adsorbent and using an oxygen flow rate of 1 liter/min, activity break-through occurred at 186 hr. The calculated number of stages was 370.

Deposition of solids is being studied using zirconia as a stand-in for the corrosion products. When preformed zirconia was slurried in a glass loop with 0.1*M* uranyl sulfate, the deposition of zirconia on the walls varied with the Reynolds number. Final solids concentration was 45 per cent of the initial concentration at a Reynolds number of 35,000 and 70 to 90 per cent at a Reynolds number of 93,000.

The operation of a hydroclone was tested in nine loop runs containing zirconia (used as a stand-in for plutonium oxide in this case) slurried in 1.4*M* uranyl sulfate at 250°C. Ninety per cent of the zirconia plated out on the walls, whereas an average of 7.5 per cent was removed by the hydroclone. Additional surface area in the form of Raschig rings had little effect on the rate of removal. The same loop was operated at 250°C for 93 hr with 1.2*M* uranyl sulfate containing 1.3 to 1.7 mg of plutonium per liter. The object was to determine plutonium adsorption in a system where the plutonium solubility was not exceeded. The distribution of plutonium indicated that the bulk remained in solution, 2.7 per cent adsorbed on the walls, and insignificant quantities were found in the hydroclone. It appears that the plating-out phenomenon is associated with the presence of precipitated solids.

Work on thorium oxide slurries for use in the blanket indicates that the firing temperature of thoria influences adsorption of fission products such as neodymium. A minimum adsorption of neodymium occurred in thoria slurries at 250°C when the calcination temperature was 1000°C.

Liquid Metal Fueled Reactor (LMFR)

For the Liquid Metal Fuel Reactor Experiment (LMFRE) program being carried out by Babcock & Wilcox Co., a reference design report[57] has presented conceptual flow sheets of the various steps. The most recent design thinking of Babcock & Wilcox favors a large (315 electrical megawatts) power plant and an externally cooled single-region reactor processed very infrequently (every 4000 days).[58] Volatile fission products are removed by degassing, and fission-product metals more noble than bismuth may be removed by a zinc-extraction process. Decontamination from the chief fission-product poisons including rare earths are considered by two alternate methods: a fused-chloride extraction process under development at BNL and a fluoride volatility process being studied at ANL.

An estimate was made of the formation of the volatile species of iodine in the LMFR bismuth fuel.[59] Reasoning based on chemical kinetics and thermodynamics indicated that the predom-

inant form would be the monoiodide of alkaline and alkaline-earth fission products. Partial pressure of iodine over the fuel solution is estimated to lie between 10^{-14} and 10^{-19} atm. On this basis it appears that iodine volatilization would be insignificant. Since numerous assumptions were made in this analysis, experimental work has been initiated to determine the vapor pressure and extent of dissociation of the iodides of elements comprising the LMFR fuel.[60]

Development has continued at BNL on the process for the removal of fission-product poisons from the uranium-bismuth fuel by fused-chloride extraction. Refined measurements have been made of salt-metal distribution coefficients for samarium, zirconium, neodymium, and uranium in the presence of various magnesium concentrations.[60] The samarium and neodymium transferred heavily to the salt phase, but zirconium transfer was only slightly greater than that of uranium. On the basis of these results, the activity coefficients of neodymium, samarium, and zirconium were estimated to be 10^{-12}, 10^{-17}, and 10^{-5}, respectively.

When LMFR fuel is treated with fused-chloride salt, a little uranium transfers to the salt phase along with the bulk of the soluble fission products. It is proposed that this uranium can be recovered from the salt by scrubbing it with bismuth containing more magnesium than fuel. To test the feasibility of this step, a series of 1-g experiments were made in which uranium distributions were measured in the system bismuth-uranium-magnesium against sodium chloride–potassium chloride–magnesium chloride–uranium chloride, no uranium being present in the metal phase initially.[61] Partition coefficients for uranium obtained in this way were found to be four to five times greater than those obtained when the uranium was initially all in the metal phase. It was also found that magnesium concentrations above 30 ppm in the metal had little effect on the coefficients. This latter effect may require some modification of the present fuel processing scheme.

The use of molten bismuth chloride–potassium chloride–lithium chloride to extract uranium and fission products from a uranium-bis-

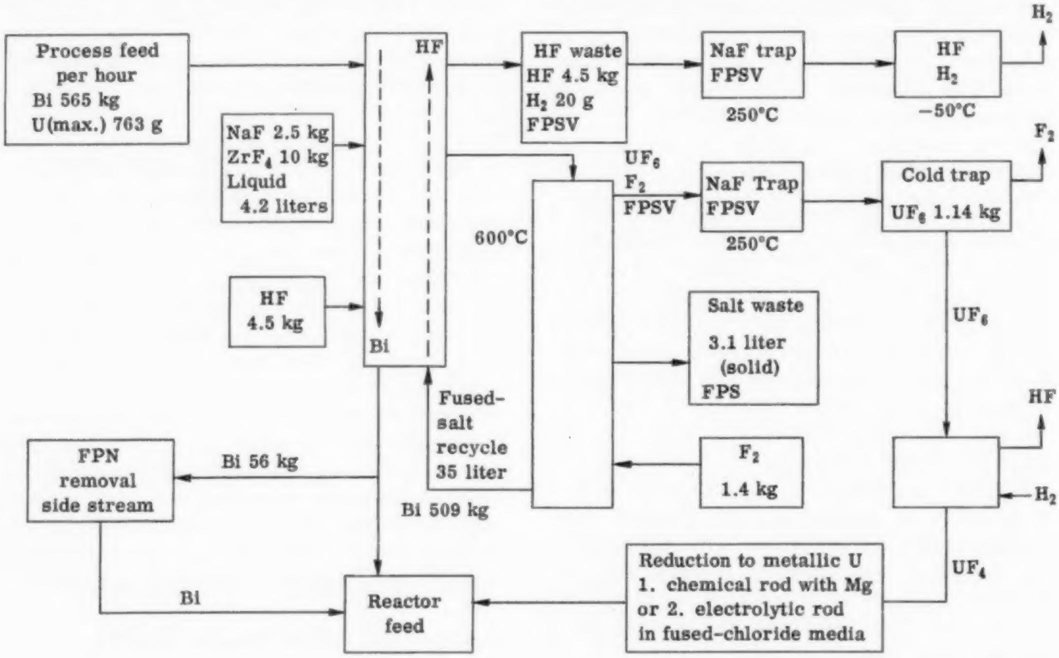
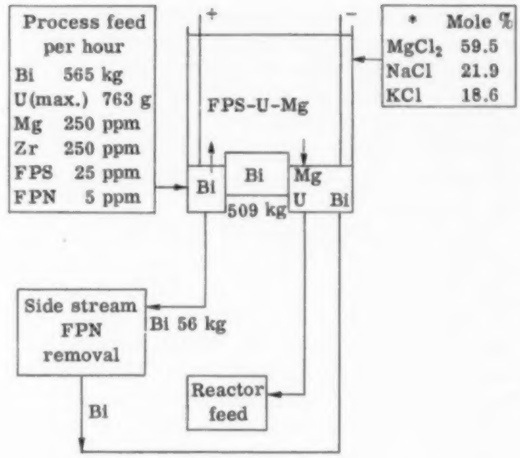


Figure 5—Fused fluoride—volatility process flow sheet for LMFR fuel processing. Data obtained from Ref. 28, p. 36.

muth liquid-metal fuel is being investigated at ORNL as a head-end step for aqueous processing.[38] In one equilibration at 550°C, a 30 wt.% solution of bismuth chloride in the fluoride eutectic was contacted with a bismuth solution of 0.7 wt.% uranium. The uranium separation factor was 300. Uranium chloride produced would be further processed by Darex and solvent-extraction steps. Partially decontaminated bismuth could be reused.

A slurry of uranium dioxide in bismuth has been proposed as a reactor fuel.[62] Knolls Atomic Power Laboratory (KAPL) experiments made with uranium dioxide–bismuth slurries at 500 to 600°C indicate that titanium is the best additive to promote the wetting of uranium dioxide by bismuth. Uniform dispersions of uranium dioxide in 10 to 12 wt.% bismuth were prepared. Loop studies indicated that at least an 8 wt.% slurry could be pumped at 450°C with an electromagnetic pump.

Work has begun at ANL on the development of alternate chemical processes for LMFR fuel processing. Two promising process flow sheets have been suggested.[63] In the first process fission products are removed from the bismuth as fluorides and extracted into a sodium fluoride–zirconium fluoride fused-salt medium. The uranium is oxidized to uranium tetrafluoride with hydrogen fluoride sparge and then to uranium hexafluoride with fluorine. Purification of the uranium hexafluoride may be accomplished by distillation if desired. The uranium is then reduced to the metal chemically or electrolytically, returned to the bismuth, and then to the reactor. A conceptual flow sheet is shown in Fig. 5. In the second process fission products are removed from the bismuth as chlorides by extraction into a fused-chloride medium. Uranium is oxidized electrolytically on a liquid-bismuth anode and deposited at a liquid-bismuth cathode. The uranium dissolved in bismuth in the cathode compartment is returned to the reactor. The noble fission products remaining in the bismuth in the anode compartment can, in part, be returned to the reactor. A portion can be extracted with liquid zinc, and the bismuth, decontaminated from the noble fission products, can be reconstituted with uranium and returned to the reactor. A schematic flow sheet of this process is presented in Fig. 6. Laboratory equipment is being designed and built to be used for experiments to evaluate these process flow sheets.



*Other chloride fused-salt systems may be feasible.

Figure 6—Fused chloride—anodic dissolution process for LMFR core feed. Quantities are based on flow per hour. Data obtained from Ref. 28, p. 36.

Tests were made on graphite as a container material for hydrofluorination of bismuth–sodium fluoride–zirconium fluoride mixtures. Experimental grades of impregnated graphite were tested to determine the dimensional changes and the degree of penetration of the melt into the graphite. Dimensional changes were small, but considerable permeation by the fused salt was evident.

Corrosion

Corrosion problems are encountered within each of the process development areas reported. Because the problems are of such a nature that specific corrosion programs can be set up and because much of the literature is reported under this heading, this section will attempt to cover the subject for all of the areas of interest.

Solvent-extraction Processes

In order to incorporate newer fuels into existing solvent-extraction plants, a number of head-end processes are being developed (see pp. 3 to 7. These processes require more than usually corrosive chemicals.

A topical report on the selection of materials for the Zircex and Darex processes was recently issued.[64] No material was found to be com-

pletely suitable for both steps of the Zircex process (chlorination and residue dissolution). Promising materials for handling the chlorination are Haynes 25 (S-816), Inconel, Illium R, and Hastelloy B; titanium or tantalum may be used for residue dissolution. For the Darex process titanium is considered the most promising material.

Titanium and Haynes 25 were exposed[25] to $5M\ HNO_3 - 2M\ HCl$ under heat-transfer conditions with a metal temperature of 135°C. Measured corrosion rates were 4 and 18 mils/month, respectively. A number of nonmetallics were also exposed to Darex solutions at room temperature. Most of those tested showed little change.

Several studies are being made on the corrosion characteristics of HNO_3-HF mixtures. It is proposed[65] to dissolve thorium and thoria-bearing fuels (after decladding) in $13M\ HNO_3 - 0.05M$ HF. Corrosion of stabilized Carpenter 20 and S.S. 17-7 PH (precipitation hardness) in the refluxed dissolver solution were 50 and 100 mils/month, respectively. Corresponding exposure times were 38 and 61 hr.

Fused-salt Volatility Process

In this process zirconium-matrix fuel assemblies are dissolved by hydrofluorinating in a fused-fluoride medium; uranium hexafluoride is then recovered by fluorinating the dissolved uranium tetrafluoride. Graphite is one of the promising materials of construction for the dissolution step. Tests with experimental impregnated graphites in hydrofluorinated sodium fluoride–zirconium fluoride at 600°C indicate that the maximum rate of dimensional change[66] is 6 mils/month. The number is high because of the nonuniformity of the graphites tested and attendant uncertainty of measurement.

Data on salt penetration into the same graphites were obtained by spectrochemically analyzing lathe turnings for sodium. The sodium content in two experimental graphites that had been exposed for 1000 hr or more indicated that the amount of salt that had penetrated the graphite was 0.05 vol.% or less. This is low compared to the 14.7 vol.% that would have been obtained if all the pores had been filled.

Laboratory tests in the hydrofluorinated fused-salt environment (sodium fluoride–zirconium fluoride) at 650°C with various metals continue to indicate the potential usefulness of nickel-molybdenum alloys.[65,67] A 430-hr test with experimental alloy INOR-1 (15 to 20 wt. % molybdenum, 0.5 wt. % aluminum, balance nickel) produced no detectable intergranular attack on penetration. The dimensional change of monel in a 1000-hr test averaged 25 mils/month in areas of highest gas velocity. Another of the nickel-molybdenum alloys, experimental alloy INOR-8 (10 to 20 wt. % molybdenum, 5 to 10 wt. % chromium, 4 to 10 wt. % iron, balance nickel) was reported in early tests to have reasonable chemical resistance to hydrofluorinated salts.

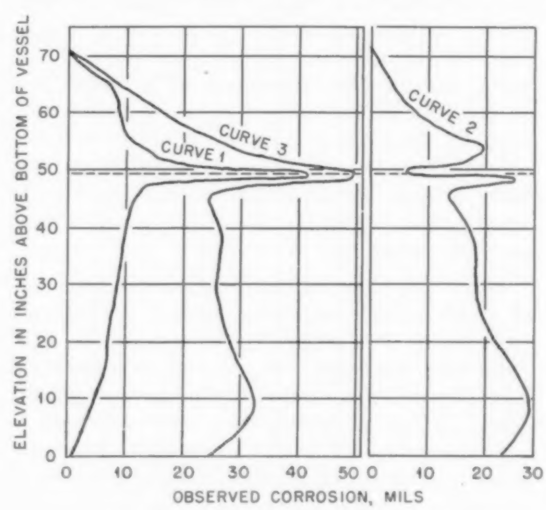


Figure 7—Corrosion of pilot plant fused-salt dissolver-fluorinator. Sodium fluoride–zirconium fluoride mixture, 600–650°C, sparged with HF for 8 hr, F_2 for 5 hr, helium for 93 hr. Total time at temperature, 120 hr. Curve 1, dimensional change of vessel wall. Curve 2, observed intergranular attack. Curve 3, total attack (Curve 1 plus Curve 2). Data obtained from Ref. 29.

The fluorination step is also receiving attention, and some data are reported.[68,69] The dissolver-fluorinator from the ANL pilot plant was recently removed from service and examined.[69] Total time at temperature was 120 hr; during 23 of these hours, the contained melt (equimolar sodium fluoride–zirconium fluoride) was sparged with hydrogen fluoride, fluorine, or bromine pentafluoride. The corrosion found is illustrated graphically in Fig. 7. A mass of gray material was found in the bottom of the dissolver-fluorinator. The nickel content was found to be about 18 per cent, of which 12 per

cent was elemental nickel. Metallography revealed metallic particles 1 mil and smaller in size. Since this was less than the average grain size of the nickel in the vessel wall, evidently the metal particles resulted from intergranular attack of the vessel, particularly in the interface region, followed by corrosion that reduced the size.

In connection with fused fluoride salt processing of bismuth fuels, the corrosion[70] of graphite by hydrofluorinated bismuth was found to be less than 6 mils/month at 600°C. Penetration of bismuth into an impregnated graphite was less than 0.002 vol.% at a depth of 40 mils from the graphite surface. A number of metal coupon tests were made in hydrofluorinated sodium fluoride–zirconium fluoride at 600°C. Molybdenum, silver, gold, and platinum had low weight changes in one-day tests.

The fused chloride salt extraction process for bismuth fuels uses a ternary eutectic of sodium chloride, potassium chloride, and magnesium chloride to which an oxidant, bismuth chloride, is added. Corrosion tests done to date include static, rocking furnace, thermal loop, and forced loop tests.[71,72] It appears that type 347 stainless steel is useful with the barren salt, perhaps with up to 1 per cent bismuth chloride addition; with over 1 per cent bismuth chloride, molybdenum is required. Type 400 stainless steels plus $2^1/_4$ chromium–1 molybdenum have some promise for contacting applications in the combined salt and bismuth environment. Stainless 347 is not compatible with bismuth. In a 1000-hr static test with bismuth plus salt including 1 per cent bismuth chloride at 500°C, tantalum was attacked both intergranularly and transgranularly. It was also brittle.

Pyrometallurgical Processing

Tantalum boride had previously been reported to be resistant to molten uranium (Vol. 1, No. 1, p. 23, of this Review). Various deposition techniques are being examined, the most recent of which is the electrophoretic method.[73] This method deposits a coating of boron from a suspension of 325-mesh boron in methanol. The boron is subsequently converted to boride by heat-treatment. Coatings produced to date have adhered well to the tantalum base metal even after an 1800°C vacuum heat-treatment. To date no corrosion tests have been made using this method of boride film formation.

Aqueous Homogeneous Reactor Processing

In corrosion experiments performed in conjunction with the HRT at Oak Ridge, it was found[74] that titanium in crevices was subjected to hydride formation and embrittlement in uranyl sulfate environments at 250°C. The specific case identified was a piece of titanium located below a stainless-steel strap in a specimen rack. It is postulated that the solution under the strap became depleted in oxygen, thus encouraging the formation of hydrogen as the cathodic reaction product. This resulted in hydride formation and subsequent embrittlement of the titanium.

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Survey of Existing Problems

A National Academy of Sciences Committee on Waste Disposal (Division of Earth Sciences) was set up at the request of the Atomic Energy Commission to study the possibilities of disposing of radioactive waste materials on land and to indicate what research was needed to determine the feasibility of various suggested solutions. Some of the background reports of this Committee have been referred to in the previous reviews.[1] The report[2] of that Committee, *The Disposal of Radioactive Waste on Land*, is now available and is excerpted in the following paragraphs. It must be noted that the report employs the term "safe disposal" in the sense in which "safe *ultimate* disposal" is normally used. Present disposal practices are "safe" though they may not be "ultimate."

> Safe disposal is defined to mean that the waste shall not come in contact with any living thing. Considering half lives of the isotopes in the waste this means for 600 years if cesium-137 and strontium-90 are present or for about 1/10th as many years if these two isotopes are removed to a sufficient degree. . . . The Committee is convinced that radioactive wastes can be disposed of safely in a variety of ways and at a large number of sites in the United States. It may require several years of research and pilot testing before the first such disposal system can be put into operation. Until such time storage in tanks will be required for waste.
>
> The cost of safe waste disposal will probably be relatively high until a great deal of research has been done and experience gained. Transportation costs have to be added to overall disposal costs. For this reason site selection for any chemical processing plant where large quantities of highly radioactive waste will be produced must be based on availability of a disposal area within economic transportation distance. Economic balance will exist between length of cooling time in tanks at the site of waste production versus cost of transportation in shielded carriers . . .
>
> It will not be possible to dispose safely of large quantities of high-level wastes in many sections of the country.

For instance, it seems highly unlikely that waste can be disposed of safely within the vicinity of New York City.

> The most promising method of disposal of high-level waste at the present time seems to be in salt deposits. A great advantage here is that no water can pass through salt. Fractures are self healing. Abandoned salt mines or cavities especially mined to hold wastes are in essence long enduring tanks. The possibility of making cavities in salt by pumping in water and removing brine is not favored (except for wastes in solid form) unless the size and shape of such a cavity can be accurately controlled. The major element of potential risk in disposal in salt is that the cavity would collapse structurally in time. Salt is a weak material and will flow. Hence, research is needed on size and shape of openings which can be relied upon to be structurally stable. The cavities should be at relatively shallow depth to avoid high confining pressures.
>
> The second most promising method seems to be in forming a silicate brick or slag which would hold all elements of the waste in virtually insoluble blocks. These could be stored in sheds on the surface in arid areas or in dry mines. . . . Disposal of the waste in porous media such as sandstones at comparatively great depth may eventually be possible. . . . The great difficulty with this potential method is that the character of the waste fluid would have to be changed drastically to permit it to disperse in the porous medium without clogging the pore space.

There also became available during this quarter a British report containing a collection of 250 unclassified references[3] on various categorized aspects of waste disposal.

Operating Experience

Savannah River Plant

At the Savannah River Plant the radioactive wastes from the Purex process are segregated[4] into three fractions:

1. *Low Activity Waste*. Aqueous sodium aluminate from the coating removal step. This

material contains about 35 per cent solids and about 0.1 per cent of the total radioactivity.

2. *High Activity Waste*. HNO_3 solution containing the bulk of the fission products and certain process reagents. This nitric solution is concentrated by evaporation and then treated with caustic soda, yielding an alkaline solution containing about 40 per cent solids.

3. *Warm or Very Low Activity Waste*. Material containing laboratory drain wastes, condensates, laundry wastes, and discard water.

The high- and low-activity waste solutions are stored separately in underground tanks that are constructed of carbon steel and encased in concrete. The high-activity fraction is stored in tanks that are equipped with cooling coils in order to remove the decay heat of the fission products. Aging for several years is required before the activity decays to the point that cooling is no longer needed.

A description of many of the physical properties of the neutralized radioactive waste solutions at Savannah River has recently been published.[5] Concentration of the stored water to 70 to 75 per cent solids has been shown to be practical. The volume reduction is about 3 to 1, and the residue solidifies rapidly as the temperature falls below the boiling point.

Essentially all the radioactive material that appears in the Savannah River Plant waste streams is stored in tanks, but a small fraction of the activity (about 1 part in 10 million) is present in the water that is removed during the concentration of the high-activity waste prior to storage. This water and other wastes are disposed of by means of seepage basins located at the plant site.

Hanford

A review has recently been made of the history and technical aspects of specific retention disposal of radioactive liquid wastes in the separation plant areas. It was recommended that the limit of the waste volume discharged for specific retention be lowered from 10 to 6 per cent of the soil column volume.[6]

As of May 1956, there were 202 ground disposal facilities at Hanford, of which 144 are in the separations area plateau.[7] The 200 area separations plants in 12 years have discharged to service disposal facilities over 20 billion gallons of essentially uncontaminated cooling water and steam condensate and to underground disposal cribs more than 450 million gallons of radioactive liquid waste, which by original operating criteria would have been stored in underground tanks.

Original estimates of the time required for ground water to travel from the 200 areas to the Columbia River determined when an impounded condition existed in the ground water under the 200 area varied between 50 and 500 years, depending on possible paths. More recent measurements taken when the ground water mound under one of the plants had decreased in height indicated a one-year travel period for water moving from the 200 east area to the Columbia River. This reduced travel time significantly lessened the anticipated effectiveness of radioactive decay in reducing the concentration of longer lived radioisotopes that might reach ground water in this area.

Ground water disposal of low-activity liquid wastes costs approximately 1 to 2 cents per gallon as compared to an average cost of 20 to 40 cents per gallon for tank storage. Underground storage tanks in the separations areas can contain 100 to 200 gallons of waste per square foot of ground surface area. Many of the ground disposal facilities in the same areas have received at least ten times this volume of waste per square foot of ground surface area without untoward effects.

Several attempts have been made to relate the radioisotope content of the Columbia River to the amounts of radioisotopes in reactor effluent water discharged to the river.[8] The results have not been consistent. Recently improved techniques, however, allow the comparison of the amounts of ten specific radioisotopes in the Columbia River at downstream points with the amounts of these radioisotopes released to the river from the reactor operations. An average depletion of 35 per cent was measured between the reactor outfalls and the Pasco and Kennewick areas. This depletion is a self-purification which may be an important factor in estimating exposures resulting from the domestic use of this water. In the first 50 miles below the reactor outfalls, about one-half the Na^{24} and Cu^{64}, two-fifths the As^{76}, one-third the P^{32}, Zn^{65}, and Np^{239}, and about one-fifth the Cr^{51} are lost.

In the operation of the Redox plant, the I^{131} emission to the stack averaged 0.11 curie/day regardless of dissolver operation, thus indicating the vessel vent system to be the princi-

pal remaining source of iodine emitted to the stack. Analysis of the caustic scrubber effluent showed that I^{131} removal at that point averaged approximately 0.01 curie/day, thereby providing strong evidence that virtually complete retention of iodine was achieved by the combined silver reactor, absorber, and caustic scrubbing system.[9]

In some experimental work relating to iodine chemistry, an iodine-air mixture was passed through 5 per cent HNO_3 solutions containing $0.01M$ mercuric ion (simulating addition of mercury to the Purex acid-removal facility). Iodine absorption was excellent and averaged 99.95 per cent for concentrations ranging from 10^{-6} to 3×10^{-9} gram iodine per milliliter of air. Somewhat poorer iodine removal was observed at $10^{-4}M$ mercury or when the iodine concentration absorbed in the HNO_3 was allowed to exceed the mercury concentration. However, iodine removal was also very good (88 to 100 per cent) even in the absence of mercury, suggesting that the mercury addition may not be needed.[6]

In some additional experimental work the efficiency of iodine removal from air by caustic scrubbing was found to be greater than 99.85 per cent under the following conditions: caustic concentration, 4 to 26 wt.%; iodine feed rate, 0.03 to 0.6 g/hr; and L/V, 0.007. Reducing the L/V to 0.0035 (1 run) reduced efficiency[10] to 91.5 per cent.

Volume Reduction

Any significant decrease in the volume of wastes to be stored in tanks is economically attractive. At Savannah River an evaporation test program using a Griscom-Russel bentube continuous unit with internal heating tubes was set up.[4] Operation of this evaporator with nonradioactive simulated plant wastes having the approximate compositions of both the low- and high-activity stored wastes was satisfactory. The tubes were designed to crack scale when subjected to heat shock. The evaporator can be operated for about 48 hr at an average heat transfer of 250 Btu/(hr)(sq ft) of heating surface, after which about 4 hr is required for descaling.

A study is being carried out at HAPO on the use of submerged combustion. Eight runs have been made on a one million British thermal unit per hour unit. Solutions of sodium nitrate and cold coating wastes were concentrated. De-entrainment factors of greater than 10^5 were measured using sodium ion as a tracer.[6]

Also at HAPO work is continuing on the destruction of HNO_3 by chemical means. It was found that 94 to 98 per cent of the free HNO_3 in a simulated first-cycle Purex aqueous waste could be destroyed[11] with the use of 1 mole of formaldehyde per 4 moles of HNO_3. This approaches the limiting theoretical stoichiometry very closely. It was also found that the deacidified product could be evaporated to about one-third the original waste volume before precipitation was observed. Drying and calcination of the concentrated waste resulted in an even smaller volume.

The behavior of fission products during the formaldehyde treatment was established by adding a spike to the feed. No activity could be found in the overhead condensate, implying decontamination factors of gross activity and a ruthenium decontamination factor greater than 10^5. This may be compared to a ruthenium decontamination factor of 10^2 to 10^4 in laboratory studies of the conventional Purex HNO_3 recovery and indicates that volatilization of fission products will not be a problem in the formaldehyde process.

Another method for HNO_3 waste treatment is the electrolytic destruction method[12]. This process is an electrolytic reduction in alkaline solution in which ammonia is produced at the cathode and oxygen at the anode. The basic flow sheet is shown in Fig. 8. The process is as follows:

1. Nitric acid waste is neutralized by sodium hydroxide. A gross fission-product decontamination factor of 2 to 10 may be obtained by removing the solids formed at this point.
2. The alkaline nitrate waste is electrolyzed in a cell similar to commercial hydrogen-oxygen cells but uncompartmented. Oxygen produced is scrubbed and released by conventional methods. Some ammonia may be released with the oxygen; however, conditions may be adjusted to keep it in solution. Only enough ammonia is produced to match the HNO_3 originally added to the system. The aqueous product is sodium hydroxide.
3. This caustic solution which may contain undestroyed nitrate is evaporated to remove water and also to remove the ammonia which is

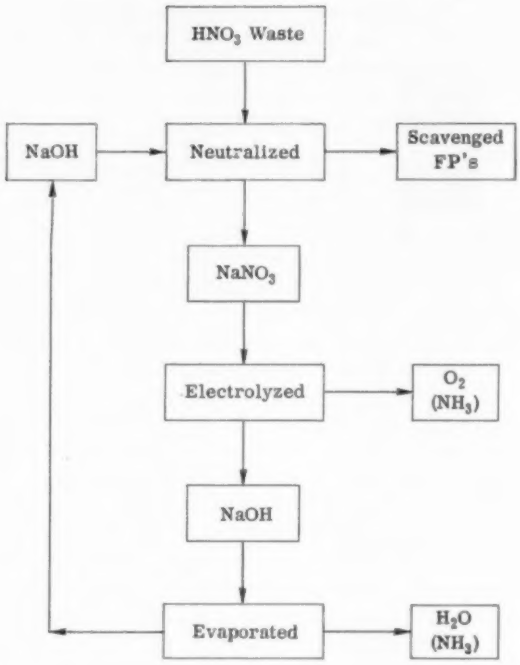

Fig. 8—Flow sheet for electrolytic destruction. Data obtained from Ref. 12, p. 14.

produced at the previous step. The distillate is dilute ammonium hydroxide that is suitable for direct disposal. The evaporator heel is simply recycled to the neutralization step.

Thus, at steady state all scavengeable fission products are removed in the first step. Since this is the net radioactive waste volume reduction, it is ultimately limited by the volume of precipitated fission products. High decontamination factors are required only at two points, water removal and electrolytic gas removal.

Process chemistry studies with small laboratory cells have shown that a large fraction of the nitrate ion in alkaline solution can be electrolytically reduced to gaseous nitrogen reduction products at current efficiencies of 95 per cent.

The total cost of the process is estimated at \$2.75 per gallon of waste processed, of which the electrical cost of the electrolysis amounted to only 23.5 cents. The basis for the cost estimate was taken as 475,000 gallons of 2.25*M* HNO_3 wastes per year. For comparison, a parallel cost estimate of waste processing by evaporation and storage resulted in a figure of \$1.34 per gallon.

Reduction to Solids

There has become available during this quarter the report of a meeting held in June 1957 at the Johns Hopkins University on the *Fixation of Radioactivity in Stable, Solid Media.* This report is more than 100 pages long and summarizes rather well the status of the various research projects in this area.[13]

Reference has been made in previous reviews in this series to the method of fluid-bed calcination of aqueous wastes. A comprehensive review of the work at the Idaho Chemical Processing Plant (ICPP) on this process is available.[14] A schematic view of the equipment in use in the pilot plant there is shown in Fig. 9. Up to the present time the calciner has been operated 2500 hr. The longest continuous run extended for 336 hr and was voluntarily terminated. A number of 100-hr or longer continuous runs have been made, all of which were voluntarily terminated. On the other hand many runs have been made with startup in the morning and shutdown 8 hr later followed by startup the following morning.

The off-gas from the ICPP calciner has been put through a silica-gel bed in an effort to effect higher decontamination factors for ruthenium. It has been found that the removal of ruthenium by the silica gel is a direct function of the silica-gel regeneration temperature.[15] This is analogous to the behavior of silica gel in air drying processes. Regeneration temperatures of 60, 100, 140, and 180°C gave maximum ruthenium decontamination factors of 170, 360, 700, and 1000, respectively, in 12-hr runs on the same silica-gel bed.

At HAPO unneutralized synthetic Purex first-cycle aqueous waste was dryed, ground to powder, and calcined[11] in a tube furnace at temperatures of 150 and 900°C. Qualitatively, volatilization of ruthenium was observed to decrease at a higher temperature or by the addition of formaldehyde vapor to the air stream passing through the furnace.

Hanford continues its interest in the gelling of wastes, a process described in Vol. 1, No. 2, of this Review. Interest is now centering on attempts to drum-dry the gelled coating wastes prior to storage.[16]

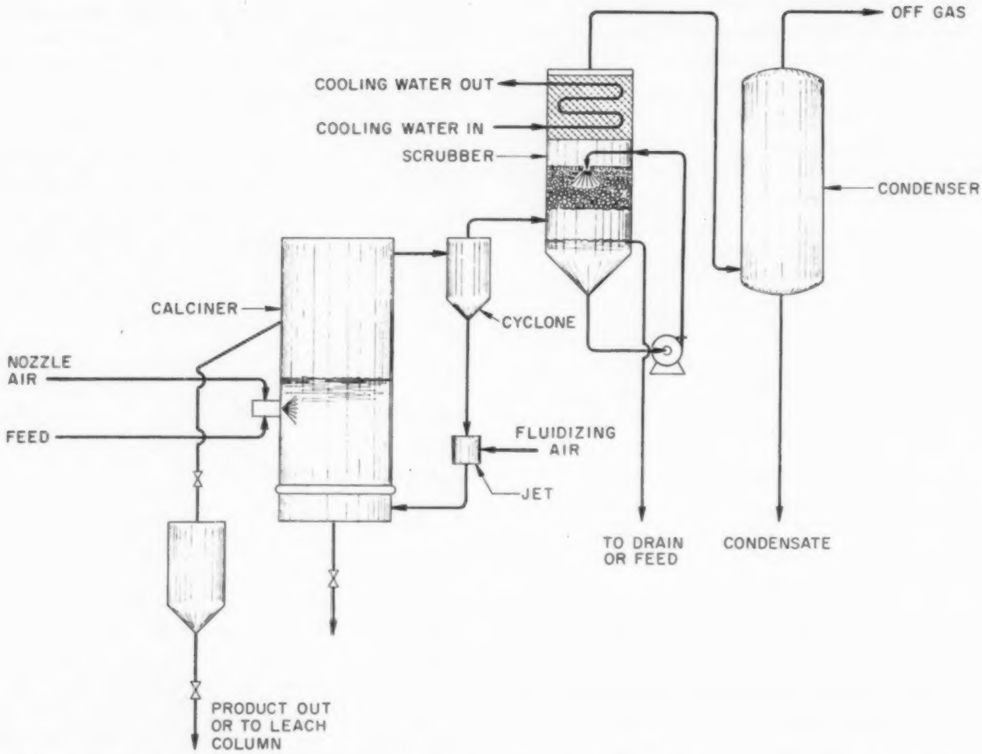

Fig. 9—Chemical Engineering Laboratory calcining equipment. Data obtained from Ref. 14, p. 7.

Hanford, Oak Ridge, and Brookhaven all continue their interest in the adsorption of activity onto clays and other naturally occurring materials. Brookhaven reports Sr^{90} decontamination factors of 1.6×10^{3} for 200 column throughputs of waste solution through a montmorillonite clay.[17]

Radioactive waste and ground water solutions passed through columns of indigenous Conasauga shale at Oak Ridge to determine the behavior of Cs^{137} show that the cesium was absorbed very effectively,[18] with a shale dissolution distribution ratio of 500. By combining coprecipitation with adsorption on shale columns, it was possible to obtain decontamination factors of 2×10^{3} for gross beta, 3×10^{3} for gross gamma, 4×10^{4} for cesium, and 2×10^{2} for ruthenium.

Removal of Specific Isotopes

The separation of specific fission isotopes from waste streams either for use or to permit some simplification of the waste storage continues to be of interest. A review of the HAPO work on the recovery of cesium with ferro- and ferricyanides has become available.[19] A final report on a fission-product separations study made by Kellex was also issued.[20] This latter report gives (1) information on the removal of strontium as an insoluble sulfate using coprecipitating agents or scavengers, (2) the removal of strontium from acid solutions using mineral exchangers, and (3) the use of mineral exchangers or adsorbers for cesium from both acid and alkaline waste solutions.

A novel method for removing strontium and cesium from aqueous fission-product wastes called "foam separation" has been reported.[21] This method takes advantage of equilibrium concentration gradients that exist in solutions containing surface-active materials. On gassing such a solution, the surface-active components collect preferentially in the foam, and their concentration there will exceed that in either the residual liquid or the original solution. This

method is particularly effective at low concentrations. Enrichment factors (foam to bulk liquid) of greater than 10 were obtained using Sr^{89} tracer in concentrations of 10^{-5} mole/liter. At 10^{-3} mole/liter the enrichment ratio was approximately 1.

The ICPP has recently reported on the recovery of fission-product Ba^{140} in kilocurie quantities from spent MTR fuel elements.[22] These fuel elements are dissolved in sodium hydroxide, and a series of precipitations are made to isolate up to 50,000-curie quantities of Ba^{140}. Liquid-solid separations are made in a special solid basket centrifuge that serves as a reaction vessel as well as a decanter. Recovery efficiency is 70 per cent; operating time per batch is 30 hr.

Less than 0.02 per cent of the total weight of a 4-kg MTR fuel assembly is Ba^{140}. The plant is designed for remote operation because activity levels are estimated to be in the order of of 10^7 r/hr. Product specifications limit the total metallic impurities to 50 mg and strontium activity to 10 curies. Inactive Ba^{138} is limited to 7 g. Products containing as much as 49,000 curies of Ba^{140} have been produced.

Isotope Production

This subject, which is not ordinarily covered by this Review, is included in this issue because some information has become available[23] on the development of isotope production in the USSR. Production of isotopes in the Soviet Union is growing steadily. Shipments of preparations containing radioactive isotopes in 1954 were 11,500; 1955, 16,000; and 1956, 23,500. During the first quarter of 1957, 8974 shipments of isotopes were delivered to consumers. A considerable portion of these shipments was delivered to Soviet industrial enterprises. For a number of years isotopes have been exported to China, Czechoslovakia, Poland, Hungary, Rumania, East Germany, Bulgaria, and other countries.

Various laboratories are entrusted with the development of methods and technology used and the synthesis of new compounds and preparations labeled with isotopes. Plans for 1958 provide for expanding output to include 360 compounds labeled with radioactive isotopes, production of 60 new compounds containing stable isotopes, and production of 137 compounds containing radioactive C^{14}. To achieve these goals, the development of a technology and of automatic equipment for the remote-control large-scale production of alpha, beta, and gamma radiation sources containing Co^{60}, Tl^{204}, Sr^{90}, Cs^{137}, Tm^{170}, Pm^{147}, Po^{210}, and other isotopes is being carried out at the present time.

As of April 1957, prices of such important isotopes as C^{14}, Sr^{90}, Cs^{137}, I^{131}, Au^{198}, and others have been cut considerably. A separate payment on packaging of products has been established which will permit cost reductions when isotopes are purchased in large quantities.

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Processing of Uranium by Fluidization

In Vol. 1, No. 1 of this Review, mention was made of the fluidized-bed denitration process for conversion of uranyl nitrate solution to uranium trioxide. This process, first demonstrated at ANL in a 6-in.-diameter calciner, is now being developed in a 10-in.-diameter unit at Mallinckrodt Chemical Works (MCW).[1] The MCW denitrator is similar to the design previously described but is heated by vertical electric heaters extending up through the bed support plate into the fluidized uranium trioxide bed. Four spray nozzles for feeding the uranyl nitrate hexahydrate (75 per cent) solution are located in the vessel wall below the bed level but above the electric heaters. For dust removal an external cyclone separator, provided with a rotary feeder to return separated fines to the calciner, is used. Sustained runs of up to 102 hr duration have been achieved at uranium trioxide production rates as high as 123 lb/(hr)(sq ft) with acceptable product purity. Operation of the reactor was not adversely affected by the 69 vertical electric heaters that occupied over 19 per cent of the calciner cross-sectional area.

In the same Review mention was made of the fluid-bed process for conversion of uranium trioxide to dioxide by hydrogen reduction.[2] Production-size units have now been installed on all the green salt lines in the process plant at Paducah, Ky. These are two-stage reactors of the type previously described. Similar units are being tested in the MCW plant at St. Louis and in the National Lead plant at Fernald, Ohio. The original MCW hydrofluorination plant design using screw reactors called for a throughput rate of 233 lb/hr of uranium tetrafluoride per reactor bank. Prior to the advent of the fluid-bed reduction reactor, various process improvements resulted in increased uranium tetrafluoride production rates up to 400 lb/hr. Using the fluid-bed reducer with modified hydrofluorination screw reactors, rates of 600 to 800 lb/hr of uranium tetrafluoride have been achieved.[3]

UF_4 Preparation by Ion Exchange and Electrolysis

A process for producing uranium tetrafluoride from uranyl nitrate solutions by wet methods has been under development.[4] The basic steps in the method, known as the Excer process, are ion exchange to convert the uranyl nitrate solution to uranyl fluoride solution, electrolytic reduction of uranyl ion to uranous with simultaneous precipitation of hydrated uranium tetrafluoride, and dehydration to green salt.

The dilute uranyl nitrate product resulting from solvent-extraction processing of irradiated uranium is fed to a cation-exchange resin where the uranyl ion is sorbed. The feed solution need not be fully decontaminated since some fission products, such as niobium, zirconium, and ruthenium, pass through the resin column as radiocolloids or anionic complexes along with the anionic fission products and nitrate. A scrub solution may be used to remove additional impurities from the resin without removing uranium. The uranium is eluted from the resin with hydrofluoric acid as a 0.5*M* uranyl fluoride solution suitable for feeding to the electrolytic cell.

The uranyl ion is reduced in the electrolytic cell in an HF-HCl solution at 90 to 110°C. The resulting uranous ion is immediately precipitated as $UF_4 \cdot \frac{3}{4}H_2O$, whereas some of the impurities and fission products remain in solution. The precipitate is separated from its mother liquor by decantation, filtration, or centrifugation, and the mother liquor is recycled to reclaim any unprecipitated uranium. The precipitate is dehydrated by heating to 400°C in an inert atmosphere.

The electrolytic cell has a flowing-mercury cathode. The anode compartment is separated

from the cathode compartment by a cation-exchange membrane diaphragm that serves the double purpose of protecting the anode from attack by fluorine and chlorine and of keeping oxygen generated at the anode from decreasing the current efficiency in the cathode compartment. The anolyte is dilute H_2SO_4.

The process is reported to be capable of producing high-purity uranium tetrafluoride from impure uranium ore leach liquors or from ore concentrates. The feed solution may be sulfate, chloride, or nitrate, depending on the source of uranium. The ion-exchange step may be anion or cation exchange, depending on the feed solution.

The process has been demonstrated at uranium production rates up to about 50 lb/day. An active program of development of larger-scale equipment is under way.

Production of Enriched Uranium Dioxide

Process and plant facilities for the production of enriched uranium dioxide for reactor fuels have recently been described by Harrington and Ruehle.[5] The production of uranium dioxide from uranium hexafluoride (the necessary starting material for enriched fuel materials) is carried out through an ammonium diuranate (ADU) intermediate. The use of the ADU intermediate has led to a uranium dioxide of particularly good ceramic properties.

Commercial manufacture is carried out in either of two enrichment ranges. With material containing up to 3 per cent U^{235}, protection against criticality accidents is obtained by limiting the quantity of material in any one batch. In the enrichment range of 20 per cent and up, all equipment is designed to provide always-safe geometry. Cylindrical vessels are limited to 5 in. diameter, and trays are restricted to a maximum of $1\frac{1}{4}$ in. thickness.

The process consists in hydrolysis of the uranium hexafluoride with a dilute ammonia solution to give a precipitate of ammonium diuranate, which is filtered, washed, and dried. The dried powder is converted to U_3O_8 by pyrohydrolyzation with steam at 800°C. This material is reduced to uranium dioxide with hydrogen at 800°C and finally ground to a fine powder in a cone mill. For some purposes, such as inclusion in a stainless-steel matrix fuel element, a high-fired product is desired. For this purpose the powdered uranium dioxide is fired for 4 hr at 1700°C in molybdenum trays in a molybdenum-wound resistance furnace and then milled and screened.

The hydrolysis step is performed by continuously feeding uranium hexafluoride vapor and aqueous ammonia (in slight excess) into a hydrolysis reactor. Heat is removed to maintain a temperature of 30 to 40°C. Filtration of low-enrichment batches is done on a rubber-lined filter press; the high-enrichment batches are filtered on stainless steel Büchner type funnels. The washed ADU is dried in an electric circulating-air oven in stainless-steel trays at 175°C. The dried and crushed ADU is loaded in Inconel or Hastelloy C trays into a muffle furnace at 800°C, and a mixture of steam and ammonia is introduced. Pyrohydrolysis and reduction are thus performed simultaneously for the large-scale low-enrichment batches. High-enrichment batches are pyrohydrolyzed and reduced in separate operations by first introducing steam, then cracked ammonia.

The top density of the ceramic type product may be controlled over the range of 1.5 to 5.0 g/cm^3 by precipitating and washing the ADU. All work with high enrichments is carried out in dry boxes that permit recovery of all dust.

Continuous Production of Uranium Metal

A batch type bomb reduction is presently used for the production of uranium metal from green salt (UF_4) by magnesium reduction. A method of producing uranium metal at lower conversion costs and high production rates for subsequent vacuum melting into ingots is being developed on a pilot scale at the Feed Materials Production Center, Fernald, Ohio.[6]

The method involves the continuous reduction of uranium tetrafluoride with magnesium metal in a helium atmosphere inside an induction-heated graphite reactor. The reduction reaction produces molten uranium and slag (MgF_2). By use of a shear plug, the molten uranium is poured through a hole in the bottom of the reactor, while the slag is allowed to flow continuously from the reactor during reduction through an outlet within the wall of the reactor.

The uranium and slag are cast into the same graphite mold, which is coated with magnesium zirconate. After the cooled derby is taken out of the mold, the slag that adheres to the top of the uranium derby is removed.

Progress to date has included a pilot-scale demonstration of the feasibility of the continuous reduction method. Reduction runs have been performed to scope the process variables and operating conditions. A reactor preheat temperature of 1510°C was found necessary for high recovery yields because of the high melting point of the slag product. The charge material was added as briquettes of uranium tetrafluoride – magnesium containing 4 per cent excess magnesium. Intermittent pouring of the molten uranium by the use of graphite stopper-rods and nozzles was tried, but the formation of uranium carbide layers on the graphite parts prevented reliable multiple pours of the uranium.

Table V-1 EFFECT OF GREEN SALT QUALITY ON REDUCTION YIELDS

Run No.	UF_4-Mg charge, %	UO_2F_2 plus AOI,* %	Calc. yield, %	Internal condition of metal product
87	175.0	3.15	97.6	Clean
74	180.0	3.36	93.2	Clean
75	152.0	3.36	95.9	Clean
69	223.5	5.10	98.5	Dirty
70	197.5	5.10	100.4	Dirty
71	180.5	7.97	94.2	Dirty
72	181.5	7.97	82.0	Dirty

*Ammonium oxalate insoluble.

The quality of the green salt was found to affect reduction yields as shown in Table V-1. When the nonmetallic impurities (UO_2F_2 and UO_2) in the green salt totaled less than 5 per cent, an average reduction yield of greater than 95 per cent of clean metal was attained. Studies to find a suitable refractory material for the reactor have been started. Magnesia, reagent-grade magnesium zirconate, and magnesia-alumina spinel showed promise as satisfactory materials.

At KAPL a new continuous process for the production of uranium by electrolytic reduction of uranium oxides in fused-salt electrolytes has been studied on a laboratory scale.[7] Unlike past electrolytic processes for uranium production, the present one is operated at temperatures that are above the melting point of uranium. Such a process has an economic advantage over processes in which uranium tetrafluoride feed is used because the necessity of preparing the fluoride is avoided. An engineering evaluation of the process was mentioned in Vol. 1, No. 1, of this Review.

The work thus far completed indicates that electrolytic reduction of uranium oxide is feasible at temperatures above the melting point of uranium metal. Although uranium has not been produced in high yield in the laboratory operations to date, higher efficiencies should be obtainable in larger scale operations.

The present work indicates that a mixture of magnesium fluoride, barium fluoride, and uranium tetrafluoride is satisfactory as a solvent electrolyte. A bath containing about 20 mole % uranium tetrafluoride was found most satisfactory. An anode current density of 3.6 amp/cm^2 was used without difficulty. Any of the major uranium oxides can be used as feed, but, since uranium trioxide is the direct product of denitration of uranyl nitrate, it would be the most desirable.

The major remaining problems are associated with the settling of the oxide in the electrolysis cell because of its low solubility and high density. In addition, materials of construction for the electrolytic cell must be thoroughly investigated. At present, graphite looks like a suitable material.

AEC Charges for Nitrate to Metal Conversions

Recently the AEC announced charges it would make for conversion of plutonium nitrate to metal. It also announced charges for conversions of uranyl nitrate to uranium hexafluoride for certain enrichments. Information on these charges is given (pp. 1 to 2).

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